honi soit qui mal y pense
DIEU ET MON DROIT

IMPERIAL AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI.

1337

JOURNAL

OF

THE CHEMICAL SOCIETY.

---

## I.—*On Essential Oils.* PART I.

By J. H. GLADSTONE, Ph.D., F.R.S.

DURING the course of the inquiry into the refraction, dispersion, and sensitiveness of liquids, which was recently undertaken by me in conjunction with the Rev. T. P. Dale, several of the hydrocarbons isomeric with oil of tu and examined.* I have since then pu much further, both in regard to the physi ties of different essential oils.

1337
IARI

The frequent adulteration of thes ith in commerce, renders it necessary to explain particularly how I came by the different specimens examined. Mr. S. Piesse, who took a scientific interest in the inquiry, supplied me, at cost price, with such samples as he believed to be quite genuine, either because he distilled them himself, or because he had full confidence in the manufacturers from whom he imported them. In this way I obtained specimens of the essential oils of bay, birch-bark, bergamot, cajeput, calamus, caraway, cascarilla, cassia, cedar, cedrat, citronella, cloves, dill, elder, Indian geranium, lavender, lemon-grass, mint, myrrh, neroli, nutmeg, orange, parsley, patchouli, peppermint, petit grain, rose, rosewood, santal-wood, thyme, verbena, wintergreen, wormwood, and a collection from the establishment of Mr. Scott, of Penang, of the oils of citronella, lemon-grass, nutmeg, and patchouli, which, being duplicates from another source, served to test at once the purity of each specimen, and the uniformity of the composition of the oil from different parts of the world.

---

* See Phil. Trans., 1863, pp. 332, 340—342.

I procured at the famous Spezieria of Santa Maria Novella at Florence, samples of the oils of anise, bergamot, lemon, myrtle, orange, and rosemary, all, I believe, distilled on the premises. I purchased also the small samples exhibited last year by Gillmeister, Cropp, and Co., of Hamburg, at the International Exhibition, namely, oils of calamus, caraway 1st distillation, and 2nd distillation, coriander, cubebs, and wormwood. Mr. J. W. Osborne, of Victoria, kindly furnished me with specimens of five of those oils which that colony displayed at the Exhibition. They were from *Atherosperma moschatum, Eucalyptus amygdalina, E. oleosa, Melaleuca ericifolia,* and *M. linarifolia.* I am also indebted to Dr. Stenhouse for allowing me to examine his specimen of laurel turpentine from a species of Ocotia from Demerara; to Mr. A. H. Church for some purified hydrocarbon from anise; and to the Chemical Society for the use of some solid essence of peppermint.

Within the last few days, Dr. J. H. Gilbert has kindly intrusted me with his specimens of two blue oils, the one from the wild chamomile (*Matricaria Chamomilla*) and the other from millefoil (*Achillea millefolium*); and Mr. E. Atkinson has given me a highly coloured specimen of patchouli from the south of France. I also wish to acknowledge the services rendered by my assistant, Mr. J. D. Holmes, especially in the chemical part of this inquiry.

My examination of these oils gave me no reason to doubt the genuineness of any of the specimens, the only sign of impurity being a little alcohol in one or two of those from Hamburg.

## CRUDE OILS.

In the following table are given some of the physical properties of the crude oils: their specific gravity at 15° 5 C. (60° F.), the refractive indices of the lines A, D, and H, (or G, where the yellowness of the liquid prevented H being seen), and their power of rotating the plane of polarization. This last property is given for a tube of the length of 10 inches. Where a shorter tube for any reason was employed, the necessary calculation has been made. Thus, oil of dill was really observed in a tube of 5 inches, when it gave

108° of right-hand rotation, but it is put down as + 206°. The same length of a solution consisting of equal weights of cane-sugar and water, gives a rotation of 105°. The temperature was noted in all the later observations of this nature, but it is not recorded, as it would necessitate another column, and it appears that the difference of a few degrees makes little perceptible change in the rotating power of such of the essential oils as have been tested for this purpose.

| Crude Oils. | Spec. Grav. at 15°·5 C. | Refractive Indices. | | | | Rotation. |
|---|---|---|---|---|---|---|
| | | Temp. | A. | D. | H. | |
| Anise | ·9852 | 16° 5 | 1·5433 | 1·5566 | 1·6118 | − 1° |
| Atherosperma Moschatum | 1·0425 | 14° | 1·5172 | 1·5274 | 1·5628 | + 7° |
| Bay | ·8808 | 18°·5 | 1 4944 | 1·5022 | 1·5420 | − 6° |
| Bergamot | ·8825 | 22° | 1·4559 | 1·4625 | 1·4779G. | + 23° |
| „ Florence | ·8804 | 26°·5 | 1·4547 | 1·4614 | 1·4760G. | + 40° |
| Birch-bark | ·9005 | 8° | 1·4851 | 1 4921 | 1·5172 | + 38° |
| Cajeput | ·9203 | 25°·5 | 1·4561 | 1·4611 | 1 4778 | 0° |
| Calamus | ·9388 | 10° | 1·4965 | 1·5031 | 1·5204G. | + 43°·5 |
| „ Hamburg | ·9410 | 11° | 1·4843 | 1·4911 | 1·5144 | + 42°? |
| Caraway | ·8845 | 19° | 1·4601 | 1·4671 | 1·4886 | + 63° |
| „ Hamburg, 1st dist. | ·9121 | 10° | 1·4829 | 1·4903 | 1·5142 | .. |
| „ „ 2nd | ·8832 | 10°·5 | .... | 1·4784 | .... | .. |
| Cascarilla | ·8956 | 10° | 1·4844 | 1·4918 | 1·5158 | + 26° |
| Cassia | 1·0297 | 19°·5 | 1·5602 | 1·5748 | 1·6243G. | 0° |
| Cedar | ·9622 | 23° | 1·4978 | 1·5035 | 1·5238 | + 3° |
| Cedrat | ·8584 | 18° | 1·4671 | 1·4731 | 1·4952 | + 156° |
| Citronella | ·8908 | 21° | 1·4599 | 1·4659 | 1·4866 | − 4° |
| „ Penang | ·8847 | 15°·5 | 1·4604 | 1·4665 | 1·4875 | − 1° |
| Cloves | 1·0475 | 17° | 1·5213 | 1·5312 | 1·5666 | − 4° |
| Coriander | ·8775 | 10° | 1·4592 | 1·4652 | 1·4805G. | + 21°? |
| Cubebs | ·9414 | 10° | 1·4953 | 1·5011 | 1·5160G. | .. |
| Dill | ·8922 | 11°·5 | 1·4764 | 1·4834 | 1·5072 | + 206° |
| Elder | ·8584 | 8°·5 | 1·4686 | 1·4749 | 1·4965 | + 14°·5 |
| Eucalyptus amygdalina | ·8812 | 13°·5 | 1·4717 | 1·4788 | 1 5021 | − 136° |
| „ oleosa | ·9322 | 13°·5 | 1·4661 | 1·4718 | 1·4909 | + 4° |
| Indian geranium | ·9043 | 21°·5 | 1·4653 | 1·4714 | 1·4868G. | − 4° |
| Lavender | ·8903 | 20° | 1·4586 | 1·4648 | 1·4862 | − 20° |
| Lemon | ·8498 | 16°·5 | 1·4667 | 1·4727 | 1·4946 | + 164° |
| Lemon-grass | ·8932 | 24° | .... | 1·4705 | .... | − 8°? |
| „ Penang | ·8766 | 13°·5 | 1·4756 | 1·4837 | 1·5042 | 0° |
| Melaleuca ericifolia | ·9030 | 9° | 1·4655 | 1·4712 | 1·4901 | + 26° |
| „ linarifolia | ·9016 | 9° | 1·4710 | 1·4772 | 1·4971 | + 11° |
| Mint | ·9342 | 19° | 1·4767 | 1·4840 | 1·5015G. | − 116° |
| „ | ·9105 | 14°. 5 | 1·4756 | 1·4822 | 1·5037 | − 18° |
| Myrtle | ·8911 | 14° | 1·4623 | 1·4680 | 1·4879 | + 21° |
| Myrrh | 1·0189 | 7°·5 | 1·5196 | 1·5278 | 1·5472G. | − 136° |
| Neroli | ·8789 | 18° | 1·4614 | 1·4676 | 1·4835G. | + 15° |
| „ | ·8743 | 10° | 1·4678 | 1·4741 | 1·4831F. | + 28° |
| Nutmeg | ·8826 | 24° | 1·4644 | 1·4709 | 1·4934 | + 44° |
| „ Penang | ·9069 | 16° | 1·4749 | 1·4818 | 1·5053 | + 9° |

| Crude Oils. | Spec. Grav. at 15°·5 C. | Refractive Indices. | | | | Rotation. |
|---|---|---|---|---|---|---|
| | | Temp. | A. | D. | H. | |
| Orange-peel | ·8509 | 20° | 1·4633 | 1·4699 | 1·4916 | + 32° |
| „ Florence | ·8864 | 20° | 1·4707 | 1·4774 | 1·4980 | + 216° |
| Parsley | ·9926 | 8°·5 | 1·5068 | 1·5162 | 1·5417G | − 9° |
| Patchouli | ·9554 | 21° | 1·4990 | 1·5050 | 1·5194G. | .. |
| „ Penang | ·9592 | 21° | 1·4980 | 1·5040 | 1·5183G. | −120° |
| „ French | 1·0119 | 14° | 1·5074 | 1·5132 | 1·5202F. | .. |
| Peppermint | ·9028 | 14°·5 | 1·4612 | 1·4670 | 1·4854 | −72° |
| „ Florence | ·9116 | 14° | 1·4628 | 1·4682 | 1·4867 | − 44° |
| Petit grain | ·8765 | 21° | 1·4536 | 1·4600 | 1·4808 | + 26° |
| Rose | ·8912 | 25° | 1·4567 | 1·4627 | 1·4835 | − 7° |
| Rosemary | ·9080 | 16°·5 | 1·4632 | 1·4688 | 1·4867 | + 17° |
| Rosewood | ·9064 | 17° | 1·4843 | 1·4903 | 1·5113 | − 16° |
| Santalwood | ·9750 | 24° | 1·4959 | 1·5021 | 1·5227 | −50° |
| Thyme | ·8843 | 19° | 1·4695 | 1·4754 | 1·4909G. | .. |
| Turpentine | ·8727 | 13° | 1·4672 | 1·4732 | 1·4938 | −79° |
| Verbena | ·8812 | 20° | 1·4791 | 1·4870 | 1·5059G. | − 6° |
| Wintergreen | 1·1423 | 15° | 1·5163 | 1·5278 | 1·5737 | + 3° |
| Wormwood | ·9122 | 18° | 1·4631 | 1·4688 | 1·4756F. | .. |

From this table it will be seen that the specific gravity of these crude essential oils does not vary much, the large majority being about 0·9. The refractive index also of the large majority lies for A between 1·46 and 1·5, while the length of the spectrum, that is, the difference between the refractive indices of H and A, or $\mu_H - \mu_A$, is generally about 0·028. But the oils of parsley, atherosperma, myrrh, wintergreen, cloves, anise, and cassia, stand out as more refractive and dispersive, and, at the same time, specifically heavier. The oil of cajeput has less influence on the rays of light than any of the others.

The column of circular polarization, on the contrary, reveals the widest differences between these essential oils, both in the degree and in the direction of the rotation; but I fear no great reliance can be placed on this characteristic for distinguishing the oils; for it has been found that the rotation of different samples of the same oil varies widely, not only in the crude state, but even when the pure hydrocarbons themselves have been examined.

Nevertheless, it is possible that some of these physical characters may be of service in detecting the fraudulent admixture of oils. Thus the addition of oil of turpentine would, in almost every instance, have the effect of lowering the specific gravity, and contracting the spectrum. Again, pure oil of bergamot has a low refraction, lower, doubtless, than those mixtures which are often sold under its name. The refractive index of D has been purposely included in the above Table, as that line can be always obtained either from daylight, or more conveniently still, from a soda flame. Any instrument maker could easily contrive a simple apparatus for testing in this way the refraction of samples of essential oils.

These crude oils were submitted to fractional distillation with the view of separating their different constituents. The hydrocarbons thus rectified were further purified by repeated distillation from sodium. The alkali-metal generally combines with the oxidized oils to form a resinous non-volatile substance; but it is impossible to say that it never produces from it a new hydrocarbon. A few of these compounds containing oxygen, for instance those of the different species of Melaleuca, may be distilled unchanged from sodium.

The following is a brief account of each of these oils:

*Anise.*—This essential oil is derived from the seeds of the *Pimpinella anisum.** It has been carefully examined by Messrs. Cahours, Laurent, and Gerhardt, and is known to consist principally of an oil containing oxygen, of the composition $C_{20}H_{12}O_2$, which has received the name *anethol.* It contains, also, a small quantity of a hydrocarbon closely resembling turpentine, which may be separated from anethol by rectifying the first portions of the distillate from sodium.

*Atherosperma moschatum.*—This is distilled from the dried bark of a tree which bears the above botanical name, and is also called the *Victorian Sassafras.* The specimen was of a pale yellow colour, and of a very peculiar odour. When distilled it began to boil at about 221° C. and passed over almost entirely at 224°C. This distillate is an oxidized oil of specific gravity 1·0386 at 20°C.

*Bay.*—This oil, from the berries of the *Laurus nobilis,* has the characteristic odour of the plant, analogous to that of cloves. The specimen examined had a brownish-yellow colour. When distilled it yielded, first, a hydrocarbon, which, when rectified repeatedly from sodium boiled at 171°C., and had a specific gravity of 0·8502 at 20°C. Two combustions were made with oxide of copper.

I. 0·3096 grm. gave 0·9975 grm. of carbonic acid, and 0·3345 grm. of water.

---

* The names of the plants from which the essential oils are obtained are taken principally from Mr. Piesse's book, "The Art of Perfumery."

II. 0·3065 grm. gave 0·9867 grm. of carbonic acid, and 0·3374 grm. of water.

These analyses agree closely together, and are sufficiently near to the formula $C_{20}H_{16}$ to show that at least the great bulk of the rectified oil was of that composition. The following are the percentage proportions:—

| | I. | II. | Calculated. |
|---|---|---|---|
| Carbon...... | 87·87 | 87·79 | 88·23 |
| Hydrogen .. | 12·00 | 12·23 | 11·77 |
| | 99·87 | 100·02 | 100·00 |

When this hydrocarbon had distilled over, the boiling point rose to 252°C., and another oil passed into the receiver. It dissolved readily in an aqueous solution of potash, from which it was thrown down by hydrochloric acid. This afforded the means of separating it perfectly from the hydrocarbon. It then had the properties of *eugenic acid*. It had the characteristic odour of that substance when fresh, and also, like it, became brown on keeping, with a peculiar alteration in the smell. Its specific gravity was 1·066 at 20°C. Its refractive index was 1·5402 for the line D, and 1·5539 for F at 18°C.: the indices for eugenic acid at the same temperature having been determined by Mr. Dale and myself at 1·5394 for D, and 1·5528 for F. To supplement the proof from these physical properties, the barium-salt was prepared, and the amount of base determined. When boiled with baryta-water, the oily body gave a solution which deposited white crystalline scales, becoming brown on exposure to air.

I. 0·287 grm. ignited in a crucible gave 0·120 grm. of carbonate of barium.

II. 0·385 grm. ignited in a crucible gave 0·165 grm. of carbonate of barium.

These yield the following percentages of barium, agreeing sufficiently well with that deduced from the formula $C_{20}H_{11}BaO_4$, eugenate of barium:—

| | I. | II. | Calculated. |
|---|---|---|---|
| Barium .... | 29·06 | 29·89 | 29·58 |

*Bergamot.*—The well-known oil obtained from the cells of the rind of *Citrus Bergamia*. Each of the specimens examined had a pale green colour. It begins to boil at about 182°C. The first portions contain a little water and acetic acid, and a hydrocarbon resembling oil of lemon. At a higher temperature liquid hydrates of the oil distil over, and a small quantity of solid matter is left in the retort.

*Birch-bark.*—This oil is produced by the dry distillation of the bark of *Betula alba.* It gives its characteristic odour to Russia leather, which is tanned with this bark. When distilled, a considerable portion came over between 171°—193°C., which, when rectified several times from sodium, boiled at 170°—171°C., and had a specific gravity of 86·26, a refractive index of 1·4681 for A at 20° C., and a dispersion of ·0291. This, in conjunction with its odour of coal-tar, led to the idea that it consisted more or less of *cymol.* To separate any essential oil of the ordinary type, hydrochloric acid gas was passed through it till it had no further effect. The liquid separated from the brown resinous mass that was formed had still an odour resembling that of cymol; when treated with fuming nitric acid, it gave a nitro-substitution product having the smell of bitter almonds. It had a refraction of 1·4661 for A at 19° C., and a dispersion of ·0287, numbers lower certainly than those obtained for cymol from oil of cumin, and from camphor, and throwing doubt on its identity with either of those forms of the hydrocarbon. It may be a product of the action of heat on the bark.

The oil that was capable of combination with hydrochloric acid was never separated in a pure state. Another liquid distilled over at a higher temperature: after repeated distillation, it retained the odour of Russia leather, but its boiling point was not constant.

*Cajeput.*—This oil, from the leaves or flower-buds of several species of *Melaleuca,* has been fully examined, especially by Max Schmidl, who finds it to consist almost entirely of a "bihydrate of cajputene" $C_{20}H_{18}O_2$.

*Calamus.*—From the bark of *Calamus aromaticus.* The two specimens of this oil had the same odour, and were slightly viscid. They did not boil till the temperature rose to 260° C., and consisted almost entirely of a hydrocarbon resembling that from oil of cubebs. Burnt with oxide of copper, 0·2685 grm. gave ·8630 carbonic acid and 0·2838 water, which give the following percentage proportions:—

| | Experiment. | Calculated. |
|---|---|---|
| Carbon .... | 87·66 | 88·23 |
| Hydrogen .. | 11·74 | 11·77 |
| | 99·40 | 100·00 |

Towards the end of the distillation, a small quantity of oil of a *deep-blue colour distils over.* This has happened in other cases also, and arises from the presence of an intensely blue body, more particularly described below under oil of wormwood.

*Caraway.*—The seeds of the *Carum Carvi* contain an essential oil, which has been frequently examined. It consists mainly of a hydrocarbon $C_{20}H_{16}$, named carvene, and an oxidized oil $C_{20}H_{14}O_2$ named carvol. The carvol was identical, but the hydrocarbon differed slightly in its physical properties in the three specimens examined. This may arise from their being taken at different periods of the distillation.

*Cascarilla.*—From the bark of a species of *Croton.* It separated on fractional distillation into two hydrocarbons, having very different boiling points, the first with an odour of oil of lemon, and almost identical in physical properties with that hydrocarbon; the second almost identical with that derived from calamus.

*Cassia.*—This oil, derived from the outer bark of the *Laurus Cassia,* consists almost wholly of an oxidized oil which is said to be cinnamic aldehyde.

*Cedar-wood.*—This oil, from the shavings of *Juniperus virginiana,* obtained in making cedar pencils, was viscid, and began to distil only at 271° C., near which point the great bulk passed over. It contains oxygen.

*Cedrat.*—From the rind of the *Citrus Medica.* It consists almost entirely of a hydrocarbon similar to that from lemons.

*Citronella.*—This is produced from the leaves of the *Andropogon Schœnanthus.* The two specimens from Ceylon and from Penang both had the same agreeable odour, and consisted almost wholly of an oxidized oil of specific gravity ·8741 at 20° C., and boiling at 200° C.

*Cloves.*—The unexpanded flower-buds of the *Caryophyllus aromaticus* yield this oil, which has been previously well examined by Bonastre and others. It contains a small quantity of a hydrocarbon, to which the formula $C_{30}H_{24}$ is assigned. The great bulk however is eugenic acid.

*Coriander.*—This oil is derived from the fruit of *Coriandrum sativum.* The specimen examined began to boil at 177° C., and between that point and 182° C. a liquid passed over in quantity, which on rectification from sodium was acted on destructively.

*Cubebs.*—The fruit of *Piper Cubeba* yields a viscid oil which when distilled from sodium boils at 260° C. and resembles the hydrocarbon from cloves. The specimen also contained a minute quantity of the blue substance already alluded to.

*Dill.*—From the seeds of *Anethum graveolens.* It contains a considerable quantity of a hydrocarbon which has a lemony odour and boils at 173° C, specific gravity ·8467. As the optical properties differed more than usual from those of turpentine, two combustions of this hydrocarbon were made.

I.—0·354 grm. burnt with oxide of copper, gave 1·1435 of carbonic acid and 0·3747 of water.

II.—0·336 grm. gave 1·0773 of carbonic acid and 0·353 of water.

These agree with the formula $C_{20}H_{16}$.

| | I. | II. | Calculated. |
|---|---|---|---|
| Carbon .... | 88·09 | 87·96 | 88·23 |
| Hydrogen .. | 11·76 | 11·74 | 11·77 |
| | 99·85 | 99·70 | 100·00 |

*Elder.*—The flowers of *Sambucus nigra* give a small quantity of an oil, my specimen of which was quite limpid, and of a pale yellow colour. It consisted principally of a hydrocarbon, closely resembling that just described.

0·4626 grm. burnt with oxide of copper, gave 1·493 of carbonic acid, and 0·4876 of water.

This shows it also to be $C_{20}H_{16}$.

| | Experiment. | Calculated. |
|---|---|---|
| Carbon...... | 88·03 | 88·23 |
| Hydrogen .. | 11·72 | 11·77 |
| | 99·75 | 100·00 |

When this oil of elder was first heated, a little water and sulphuretted hydrogen came off. The residue in the retort, after the separation of the hydrocarbon, solidified, and consisted principally of a white solid substance, sparingly soluble in alcohol, very soluble in ether, crystallising on evaporation; it is not soluble in potash or ammonia.

*Eucalyptus amygdalina.*—The oil, which exists in large quantity in the leaves of this tree, was found to consist chiefly of a hydrocarbon, analogous to turpentine, and resembling that liquid in its odour.

0·2692 grm. burnt with oxide of copper, gave 0·8708 of carbonic acid, and 0·2865 of water.

This agrees with the formula $C_{20}H_{16}$.

| | Experiment. | Calculated. |
|---|---|---|
| Carbon...... | 88·22 | 88·23 |
| Hydrogen.... | 11·82 | 11·77 |
| | 100·04 | 100·00 |

*Eucalyptus oleosa.*—The leaves of this tree or shrub yield an oil, the principle constituent of which resembles oil of cajeput in its physical properties.

*Indian Geranium.*—This oil seems to be the same as that termed elsewhere "East Indian Grass oil," which is said to be produced from *Andropogon Ivaracusa.* The specimen consisted of a mixture of liquids, from which it was found very difficult to isolate any one with a fixed boiling point.

*Lavender.*—From the flowers of *Lavandula vera.* This oil has been frequently examined, and is said to contain a hydrocarbon of the usual composition, and camphor; but it was difficult to separate these in the specimen examined.

*Lemon.*—The essential oil of the rind of *Citrus Limonum* has been fully examined by different chemists. It is principally composed of a hydrocarbon $C_{20}H_{16}$. Its purity cannot be depended on in England, and therefore I have examined no specimen except the one obtained direct from the Dominican Friars.

*Lemon-grass.*— The *Andropogon Nardus* yields this essential oil, which from its odour is frequently called oil of verbena. The two specimens examined, one from Ceylon, and the other from Penang, agreed in character, and appeared scarcely distinguishable from citronella.

*Melaleuca ericifolia.*—The oil distilled from the leaves of this plant closely resembles oil of cajeput.

*Melaleuca linarifolia.*—This oil, also from the leaves, is of the same general character as the preceding.

*Mint.—Mentha viridis* yields this oil, which was found to contain a hydrocarbon almost identical with oil of turpentine in odour and other physical properties, mixed with an oxidized oil, to which is due the peculiar smell of the plant. It boils at 225°C.; its specific gravity is 9·515, and it was found to be isomeric with carvol. It should therefore, by analogy, be called menthol.*

*Myrtle.*—Many parts of the *Myrtus communis* contain this oil. Three quarters of the specimen distilled over between 160°—176°C. leaving a reddish-brown residue, which evolved sulphuretted hydrogen. The distillate rectified as usual proved to be a hydrocarbon $C_{20}H_{16}$, of rather high specific gravity, with an odour resembling that of the hydrocarbon from bay.

0·3205 grm. burnt with oxide of copper yielded 1·0265 carbonic acid and 0·3340 water, which give the following percentage:—

| | Experiment. | Calculated. |
|---|---|---|
| Carbon...... | 87·68 | 88·23 |
| Hydrogen.... | 11·58 | 11·77 |
| | 99·26 | 100·00 |

*Myrrh.*—Procured by the distillation of the gum-resin from *Balsamodendron Myrrha.* The specimen was very viscid and dark, in colour brownish-green. It began to boil at about 266° C., giving an oxidized oil, which resinified very rapidly, and retained its greenish colour and strong smell of myrrh, after repeated rectification.

*Neroli.*—The essential oil of the flowers of *Citrus Aurantium.* The two specimens of this orange-flower oil were reddish-yellow, and when dissolved in alcohol gave a fluorescent solution, the surface-blue resembling that of quinine-salts, and being also produced mainly by the extreme rays of the spectrum. It was separated by distillation into two oils—the one boiling at 173° C., and closely resembling the hydrocarbon from bergamot, while the other, which appeared to be an oxidized oil, was not obtained with a fixed boiling point. The fluorescence, and the peculiar odour of the orange flower are due to the latter. It is slightly soluble in water.

*Nutmeg.*—From the seed of *Myristica aromatica.* The three specimens examined consisted of varying proportions of a hydrocarbon resembling carvene, and an oxidized oil with the boiling point 224° C., and sp. gr. ·9466. As it closely resembles carvol and menthol in its properties, it may by analogy be named myristicol.

---

* Dr. Oppenheim has suggested this as one of the new names of camphor of peppermint; but the other name *mentholic alcohol* is more consonant with his theory.

0·406 grm. of the hydrocarbon yielded 1·3074 grm. carbonic acid, and 0·435 grm. water.

| | Experiment. | Calculated. |
|---|---|---|
| Carbon...... | 87·81 | 88·23 |
| Hydrogen .. | 11·90 | 11·77 |
| | 99·71 | 100·00 |

*Orange-peel.*—The oil contained in the peel of *Citrus Aurantium* is known to consist almost entirely of a hydrocarbon of the usual type, which has been named Hesperidene. A small quantity of a solid crystalline substance was also obtained.

*Parsley.*—From the seeds of *Apium Petroselinum.* The crude oil was viscid, and of a brownish-green colour. It contained a small quantity of a hydrocarbon of the usual composition; but there remained in the retort a much larger amount of a brown resin insoluble in potash, with a very disagreeable smell.

*Patchouli.*—This very powerful and characteristic odour is derived from the leaves and stems of *Pogostemon Patchouli* (Lindley) or *Plectranthus crassifolius* (Burnett). Both the Indian and Penang specimens were brownish-yellow, and slightly viscid. They began to boil only at 257° C., at which temperature nearly all distilled over, but towards the end the thermometer rose much higher, and the distillate contained the blue substance already noticed. That which passed over previously was found to be a hydrocarbon analogous to that from cubebs.

*Peppermint.*—This is obtained by distilling *Mentha Piperita.* Both the English and Italian specimens were found to contain a hydrocarbon, which could be separated from the oxidized compounds by means of sodium. It had physical properties differing little from those of the hydrocarbon from bay. No solid camphor was obtained from either.

The solid camphor of peppermint has been fully described by Oppenheim. Its optical properties, when melted, may be found in Phil. Trans., 1863, p. 341. The following comparison has also been made :—

| | Temp. | Sp. gr. | Refr. D. |
|---|---|---|---|
| Solid camphor .... | 16° | 0·9383 | 1·5070 (about) |
| Melted camphor .. | 43° | 0·8786 | 1·4505 |

*Petit Grain.*—Under this name is sold an oil derived from the leaves and young unripe fruit of the orange-tree. It consists mainly of a hydrocarbon, probably identical with that from oil of neroli.

*Rose.*—This essential oil, or otto as it is termed, is obtained from the flowers of *Rosa centifolia.* It is a solution of a solid crystallizable body in an oxidized oil, which has a boiling point of 216° C., and a specific gravity 881 at 20° C.; crystals of the other constituent may be generally seen floating about in the oil, especially in cold weather. This solid is said to be a hydrocarbon. It is only slightly soluble in alcohol, which affords the means of completely separating the oil from it, but it has a great power of condensing ether vapour, and thus forming an ethereal solution.

*Rosemary.*—From the *Rosmarinus officinalis.* The oil was found to consist almost wholly of a hydrocarbon resembling that from myrtle.

*Rosewood.*—Obtained from the wood of *Convolvulus scoparius.* This oil was slightly viscid, and did not boil till the temperature reached 249° C., at which temperature four-fifths passed over. The rectified oil had an odour suggesting that of roses and santal-wood, and on combustion proved to be of the usual composition. 0·377 grm. gave 1·209 of carbonic acid, and 0·3963 of water.

| | Experiment. | Calculated. |
|---|---|---|
| Carbon...... | 87·46 | 88·23 |
| Hydrogen .. | 11·68 | 11·77 |
| | 99·14 | 100·00 |

This oil is sometimes called by the name of *Rhodium.*

*Santal-wood.*—Distilled from the wood of *Santalum album.* The oil is viscid and yellow; on fractional distillation, it nearly all passes over at 293° C., giving a liquid which contains oxygen.

*Thyme.*—This oil from the *Thymus Serpyllum* is deep red in colour. The specimen examined was principally composed of a hydrocarbon like that of turpentine. It contained little if any of the thymol, $C_{20}H_{14}O_2$, which has been described by Doveri and Lallemand, as occurring in this essential oil. The hydrocarbon has been named thymene.

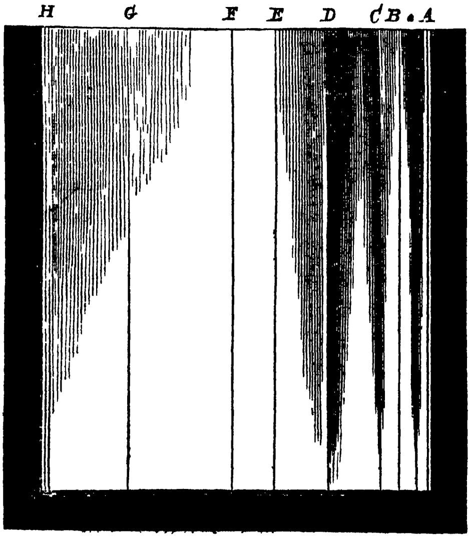
*Turpentine.*—This oil, from various species of *Pinus* has been the subject of innumerable researches. It is well known to consist of a hydrocarbon $C_{20}H_{16}$, holding in solution resins produced by oxidation.

*Verbena.*—From the *Aloysia citriodora.* The specimen was red in colour; on distillation it yielded an oxidized oil similar to that from lemon-grass, which is often called in commerce "Verbena," from the analogy of its odour. A large proportion of resinized products was left in the retort, and evolved sulphuretted hydrogen when heated.

*Winter-green.*—The leaves of *Gaultheria procumbens* yield this oil, which has been examined by Cahours. It contains a small quantity of a hydrocarbon of the usual composition, named gaultherilene, and a large proportion of another liquid which is salicylate of methyl.

*Wormwood.*—From *Artemisia Absinthium.* The oil had a dark greenish-brown colour. On distillation, it yielded a hydrocarbon like turpentine, an oxidized oil said by Leblanc to be $C_{20}H_{16}O_2$, and the blue substance already referred to.

The specimen from Hamburg contained a considerable amount of this blue body, which distils over with the last portions, and



which I have not yet succeeded in separating from the oils of high boiling point that have always accompanied it. It appears not to be attacked by sodium, but at each distillation it diminishes in quantity, and leaves a resinous mass in the retort. It dissolves in ether, alcohol, benzol, and essential oils. Its solution in alcohol is neutral to test-paper. When burnt with soda-lime it evolved ammonia, but when decomposed with fuming nitric acid it gave no trace of sulphuric acid. It has a most intense colour, appearing almost black when as pure as I have succeeded in obtaining it. Its solution in oils or alcohol, when examined by means of the hollow wedge and prism, gives the very characteristic spectrum represented in the annexed diagram. It first absorbs the orange-yellow rays near D, and afterwards the greenish-yellow, and the orange at C. At a particular depth it transmits the red rays anterior to A, absorbs those between a little beyond A and *a*, transmits the red from *a* to about C, where a dark band occurs, and thence again to about midway between C and D. From this point to D there seems to be complete absorption, then a bright space followed by a darkening of the greenish rays, but it is clear again from about E till we approach G, beyond which line little light is transmitted. At a greater depth nothing is suffered to pass, except the greenish-blue rays, and the extreme red-band. Acids and alkalis alter the colour greatly, converting it generally into a green.

It is proposed to give this blue neutral colouring matter the name of cœrulein.

Since the above was written, Mr. Piesse has sent to the Chemical Society a short description of this blue oil, and Dr. Gilbert, hearing that I was engaged on the subject, kindly offered me two fine specimens which had been prepared for him twenty-three years ago, and were still magnificently blue. On distilling that from *Matricaria Chamomilla*, I was able to separate and purify a small quantity of a hydrocarbon, with boiling point and optical properties like those of the hydrocarbon from lemon or dill, while at the same time there began to pass over an oxidized oil, the boiling point of which seemed to lie somewhere about 200° C., but it was never obtained free from cœrulein; on continuing the distillation, a more and more intensely blue oil came over, the thermometer rising above 320°, when there was left in the retort a brown resin insoluble in alcohol, but very soluble in ether. On repeated distillation, the blue compound was more and more concentrated, but the boiling point always had a considerable range.

As yet I have not succeeded in devising any means of ascertaining whether the blue oil thus obtained was almost pure cœrulein, or whether it was mainly an oil of high boiling point holding in solution some of the colouring matter; but my opinion inclines to the latter view, principally on this ground: if a portion of the distillate which passed over at a high temperature but is not very blue, be treated with sodium, a strong action ensues, and a more volatile colourless oil is produced, having a peculiar odour suggesting that of rue. Now, if a portion of the most concentrated blue liquid be cohobated with sodium, the same oil apparently is produced in considerable quantity.

The most concentrated blue oil obtained from this source agreed with the blue substance described above in every particular, excepting that it was not turned green by dilute acids and alkalis.

Its odour resembles that of caoutchine; it dissolves readily in glacial acetic acid, and in bisulphide of carbon; it is not decolorized by sulphurous acid, sulphuretted hydrogen, or bromine-water; it does not attach itself to animal charcoal, nor does it dye wool, cotton, or silk. It gave the following refractive indices:—

| Temperature. | Red band. | Blue band. |
|---|---|---|
| 9°C. | 1·5076 | 1·5330 |

The specimen from *Achillea millefolium* yielded a similar blue oil, distilling over at a very high temperature, and a resin containing a substance that was insoluble in alcohol, but soluble in ether, from which it could be obtained in tufts of crystals on evaporation. This blue substance was clearly the same as that from other plants.* Like them it gave indications of ammonia, or some volatile alkali, when it was heated with soda-lime, but the intensely blue oil yielded, in each instance, little more than a trace. It is hard to say whether this is to be attributed to the nitrogenized body being present in very small quantity, or to the difficulty of decomposing it. When special precautions were taken, a portion of blue oil was still found to escape destruction, and to condense in the small tube of the hydrochloric acid apparatus. When diluted with a hydrocarbon, this blue substance may be distilled from sodium, but it is slowly attacked by it even at the ordinary temperature.

---

* Sir David Brewster examined these specimens of Dr. Gilbert's optically many years ago, and noticed the absorption at *a*.

Mr. Piesse calls this blue oil *azulene*; but the name azuline has long been appropriated to one of the colouring matters derived from coal-tar. I am told that there is a blue pigment prepared by Winsor and Newton which is known as cœrulein.

I hope to revert to this subject if fortunate enough to get a sufficiency of the blue oil.

### The Hydrocarbons.

From the preceding descriptions it appears that there exists a hydrocarbon of the formula $C_{20}H_{16}$, or some multiple of that, in the essential oils of anise, bay, bergamot, calamus, caraway, cedrat, cloves, cubebs, dill, elder, Eucalyptus amygdalina, lemon, myrtle, neroli, nutmeg, orange-peel, parsley, rosemary, rosewood, thyme, turpentine, and wintergreen; and the oils of cascarilla, mint, patchouli, peppermint, and wormwood, contain hydrocarbons, which resemble so closely some of the preceding in their physical properties, that an ultimate analysis by combustion seemed unnecessary to establish their composition.

The following Table gives several physical properties of these hydrocarbons after they had been frequently rectified from sodium. Dr. Stenhouse's laurel-turpentine is added to the list, and so are samples of colophene and terebene. They are arranged according to their specific gravities at 20° C. The column headed "Dispersion at 20° C." gives the difference between the refractive indices of the lines H and A. The sensitiveness is the amount of diminution of the refractive index when the temperature rises 10° C.; it is calculated for the line A, and the number 48 is a short expression for 0·0048 (see Phil. Trans. 1863, p. 325). The "specific refractive energy" is the refractive index, minus unity, divided by the density. In the present table it is taken for A: that is, the column represents $\frac{\mu_A - 1}{D}$

| Source of hydrocarbon. | Specific gravity at 20° C. | Boiling point. | Refractive index A, at 20° C. | Dispersion at 20° C. | Sensitiveness. | Specific refractive energy. | Rotation. |
|---|---|---|---|---|---|---|---|
| Orange-peel | ·8460 | 174°C | 1·4645 | ·0277 | 48 | ·5490 | + 154 |
| „ Florence | 8468 | 174° | 1·4650 | ·0281 | 49 | ·5491 | + 260 |
| Cedrat | 8466 | 173° | 1·4650 | ·0280 | 49 | ·5492 | + 180 |
| Lemon | ·8468 | 173° | 1·4660 | ·0280 | 49 | 5502 | + 172 |
| Bergamot | ·8466 | 175° | 1·4619 | ·0295 | 49 | ·5456 | + 76 |
| „ Florence | ·8464 | 176° | 1·4602 | ·0287 | 48 | ·5437 | + 82 |
| Neroli | ·8466 | 173° | 1·4614 | 0291 | 47 | ·5450 | + 76 |
| Petit grain | ·8470 | 174° | 1 4617 | ·0282 | 46 | ·5439 | + 60 |
| Caraway, Hamburg, 1st dist. | ·8466 | 176° | 1·4645 | ·02-6 | 48 | ·5486 | + 180 |
| Dill | 8467 | 173° | 1·4646 | ·0288 | 46 | ·5486 | + 242 |
| Cascarilla | ·8467 | 172° | 1·4652 | ·0305 | 49 | ·5494 | 0 |
| Elder | 8468 | 172° | 1·4631 | ·0269 | 47 | ·5468 | + 15 |
| Bay | 8508 | 171° | 1·4542 | ·0260 | 47 | ·5338 | — 22 |
| Gaultherilene | ·8510 | 168° | 1·4614 | ·0271 | 49 | ·5422 | .. |
| Nutmeg | ·8518 | 167° | 1·4630 | ·0284 | 47 | ·5435 | + 49 |
| „ Penang | ·8527 | 166° | 1 4634 | ·0274 | 49 | ·5434 | + 4 |
| Carvene | ·8530 | 166° | 1·4610 | ·0261 | 48 | ·5440 | — 20 |
| „ Hamburg, 2nd dist | ·8545 | .. | 1·4641 | ·0263 | 48 | ·5431 | + 86 |
| Wormwood | ·8565 | 160° | 1·4590 | 0253 | 47 | ·5359 | + 46 |
| Terebene | ·8583 | 160° | 1·4670 | ·0275 | 48 | ·5440 | 0 |
| Anise | ·8580 | 160° | 1·4607 | ·0268 | 47 | ·5368 | .. |
| Mint | ·8600 | 160° | 1·4622 | ·0255 | 48 | ·5374 | + 30 |
| Peppermint | ·8602 | 175° | 1·4577 | ·0267 | 47 | ·5321 | — 60 |
| Laurel turpentine | ·8618 | 160° | 1·4637 | 0260 | 47 | ·5380 | + 94 |
| Thyme | ·8635 | 160° | 1 4617 | ·0282 | 48 | ·5346 | — 75 |
| Turpentine I | ·8644 | 160° | 1·4612 | ·0250 | 47 | ·5335 | + 48 |
| „ II | ·8555 | 160° | 1·4590 | ·0256 | 47 | ·5365 | — 87 |
| „ III | ·8614 | 160° | 1·4621 | ·0249 | .. | ·5364 | — 90 |
| Turpentine IV | ·8600 | 160° | 1·4613 | ·0254 | 47 | ·5364 | — 88 |
| Eucalyptus amygdalina | ·8642 | 171° | 1·4696 | ·0323 | 49 | ·5434 | — 142 |
| Myrtle | ·8690 | 163° | 1·4565 | ·0248 | 47 | ·5253 | + 64 |
| Parsley | ·8732 | 160° | 1 4665 | ·0291 | 46 | ·5355 | — 44 |
| Rosemary | ·8805 | 163° | 1·4583 | ·0241 | 46 | ·5205 | + 8 |
| Cloves | ·9041 | 249° | 1·4898 | ·0284 | 45 | ·5417 | .. |
| Rosewood | ·9042 | 249° | 1·4878 | ·0277 | 45 | ·5395 | — 11 |
| Cubebs | ·9062 | 260° | 1·4950 | ·0302 | 41 | ·5462 | + 59 |
| Calamus | ·9180 | 260° | 1 4930 | ·0322 | 42 | ·5370 | + 55 |
| „ Hamburg | ·9275 | 260° | 1·4976 | ·0337 | 43 | ·5365 | + 22 |
| Cascarilla | ·9212 | 254° | 1 4926 | ·0307 | 42 | ·5347 | + 72 |
| Patchouli | ·9211 | 254° | 1·4966 | ·0274 | 42 | ·5391 | .. |
| „ Penang | ·9278 | 257° | 1·4963 | ·0275 | 44 | ·5349 | — 90 |
| „ French | ·9255 | 260° | 1·5009 | 0262 | 42 | ·5412 | .. |
| Colophene | ·9391 | 315° | 1·5084 | ·0309 | 41 | ·5413 | 0 |

It will be seen at once that these hydrocarbons divide themselves into two great groups, the line of separation being between those from rosemary and cloves. The first group, with a lower specific gravity, has always a far lower boiling point, a smaller index of refraction, and a higher sensitiveness. It has also on the whole a smaller dispersion. The specific refractive energy, however, of the two groups is about the same. It may also be noted generally of the hydrocarbons of the first group, that they are more limpid, and dissolve more freely in aqueous alcohol.

And these large groups are capable of subdivision. The first ten hydrocarbons in the Table resemble one another very closely. Indeed, it is probable that the three which are derived from the peel of the orange, citron, and lemon respectively, should be considered as identical rather than isomeric; and it is not unlikely that some of the others are the same body from different plants. Gaultherilene, carvene, and the hydrocarbon from nutmeg, form a small group, if indeed they are not identical. The hydrocarbons from wormwood, anise, thyme, mint, and laurel turpentine, group with ordinary turpentine; bay, myrtle, and rosemary stand alone, each having a low refraction and dispersion, but they differ much in specific gravity. Peppermint is somewhat intermediate in its properties. Terebene and the hydrocarbons from parsley and Eucalyptus amygdalina give high refractive indices. It is possible that some of these last contain a small quantity of some hydrocarbon of another type, but nearly the same composition.

Again, the second large group with the higher specific gravities is capable of subdivision. The hydrocarbons from cloves and rosewood appear nearly, if not quite, identical in properties, and are certainly different from patchouli, calamus, and cascarilla.

Colophene differs from the second large group in much the same way as that differs from the first, though to a smaller extent.

All the members of the first great group, with the boiling points included between 160° and 176°C., will have the formula $C_{20}H_{16}$, which is usually assigned to oil of turpentine on the ground of its vapour-density, and compounds with the hydracids.

All the members of the second great group, with boiling points included between 249° and 260°C., will have the formula $C_{30}H_{24}$, which is assigned to oil of cubebs from its compound with hydrochloric acid.

Colophene, with a boiling point of 315°C., has long had the formula $C_{40}H_{32}$ assigned to it.

The specific refractive energy is a property of bodies intimately connected with their ultimate composition, and it might be expected that, notwithstanding diversities of boiling point and density, this property would be the same for the different isomeric hydrocarbons. Yet though the differences are not great, they seem to be real, for the lemon group is uniformly about ·549, and the turpentine group about ·536.

Nor are these differences diminished, if we reckon the specific refractive energy, not for the line A, but for the theoretical limit of the spectrum, so as to get rid of the influence of dispersion as much as possible. The following table gives the calculation for six hydrocarbons, which may be considered typical ones:

| Source of hydrocarbon. | Spec. refr. energy of limit. |
|---|---|
| Orange-peel. | ·5385 |
| Nutmeg. | ·5335 |
| Turpentine. | ·5272 |
| Cloves. | ·5346 |
| Calamus. | ·5264 |
| Colophene. | ·5314 |

It is worthy of remark that this property forms no distinction between the three great groups, the specific refractive energies of the hydrocarbons from nutmeg and cloves being practically the same, and closely resembling that of colophene.

There can be no doubt that hydrocarbons exist isomeric with oil of turpentine, but having a boiling point of 173°C., or thereabouts, and a specific gravity of ·846, but it is just conceivable that the higher refraction of the lemon group may, after all, be due to the presence of a small quantity of some body containing a larger proportion of carbon, and which cannot be separated by distillation, a suspicion that the recorded ultimate analyses rather tend to support.

In this classification of isomeric hydrocarbons no regard has been paid to the phenomena of circular polarization. This has arisen from the fact that different samples of the same hydrocarbon resembling one another closely in every other physical property, frequently differ in this. The above Table affords several instances. We need not be astonished, therefore, at wide differences between hydrocarbons, which, in other respects, are closely analogous, but which are derived from different species or genera of plants. Yet on looking down the column we can hardly fail to remark that the great lemon group is characterized by the highest numbers, and that they are always + or right-handed, with the exception of the hydrocarbon from cascarilla which belongs to this group, and actually has no influence at all on the plane of polarization.

The pure hydrocarbons have rarely powerful odours, and it is often difficult to remove every trace of the oxidized compounds, to which the characteristic fragrance of the essential oils is generally due. Yet the odour of these liquids affords some support to the classification founded on other properties. Those which have the specific gravity 0·846 emit a more or less lemony odour when freshly distilled, and some of those which resemble closely oil of turpentine in their general characters, resemble it also in this respect.

As this communication has already extended to a considerable length, my observations on the oxidized oils will be reserved for some future occasion, when I hope also to enter more fully into the chemical and physical history of some of these hydrocarbons.

## II.—*On the occurrence of Vanadium in Pig-iron smelted from the Wiltshire Oolitic Iron-ore.*

By Edward Riley, F.C.S.

Some time since samples of pig-iron were submitted to me from two different iron-works in Wiltshire, viz., the Seend and the Westbury. Silicium, sulphur, and phosphorus were the only ingredients whose percentages were required to be determined. To estimate these, the usual methods of analysis were employed, viz., oxidising the pig, in small fragments, with fuming nitric acid, adding occasionally a little concentrated hydrochloric acid. The solution was then evaporated to dryness, and heated; the mass then redissolved in strong hydrochloric acid, and the silica separated, the sulphur and phosphorus being determined as described in the Journal of the Society, vol. xvi., page 390 and 391. The following results were obtained :—

The samples of pig examined were all grey, and numbered from No. 1, best foundry, to No. 3; No. 4, best forge, to No. 6 pig, from Seend works.

### TABLE I.

| No. | Grains of pig taken. | Silica obtained. | Residue by HFl and $SO_4H$. | $BaO.SO_3$. | $2MgO.PO_5$. |
|---|---|---|---|---|---|
| 1 | 63·14 | 6·38 | ·05 | ·165 | 1·94 |
| 2 | 63·72 | 5·03 | ·08 | ·360 | 2·070 |
| 3 | 61·94 | 4·315 | ·09 | ·435 | 2·125 |
| 4 | 62·41 | 4·34 | ·075 | ·895 | 1·600 |
| 5 | 62·62 | 3·11 | ·085 | ·730 | 2·055 |
| 6 | 60·38 | 2·87 | ·050 | 1·095 | 1·920 |

Analyses 5 and 6 repeated.

### TABLE IA.

| | | | | | |
|---|---|---|---|---|---|
| A5 | 23·82 | 1·335 | ·16 | ·215 | ·74 |
| B6 | 27·515 | 1·525 | ·175 | ·46 | ·87 |

In analyses A5, B6, the oxide of iron was dissolved in the dish in which the first solution of the pig had been evaporated to dryness. The separation of the iron from the silica was not so complete as in the other analyses, when the oxide of iron was detached from the dish and transferred into a beaker in which the oxide was boiled for several hours, the beaker being well covered with a large watch glass. This process is always necessary to separate oxide of iron from silica, and to obtain the silica nearly white after burning. Two samples, No. 1 and No. 5 pig-iron, were from the Westbury Iron Works.

### TABLE II.

| Number. | Grains of pig taken. | Silica obtained. | Residue by HFl & $SO_4H$ | $BaO.SO_3$ | $2MgO.PO_5$ |
|---|---|---|---|---|---|
| 5 | 61·28 | 4·23 | ·43 | ·20 | 3·92 |
| 5 | 62·39 | 3·545 | ·275 | ·37 | 4·095 |

### TABLE III.

***Results: Silicium, Sulphur, and Phosphorus per cent.***
***Wiltshire Pig Iron (Grey) from Seend.***

| No. | Silicium. | Sulphur. | Phosphorus. | |
|---|---|---|---|---|
| 1. | 4·717 | ·036 | ·867 | Foundry Pig. |
| 2. | 3·659 | ·077 | ·917 | |
| 3. | 3·909 | ·096 | ·968 | |
| 4. | 3·140 | ·196 | ·724 | Forge Pig |
| 5. | 2·257 | ·160 | ·926 | |
| 6. | 2·197 | ·248 | ·898 | |

## Table IV.

### *Wiltshire Pig Iron (Grey) from Westbury.*

| No. | Silicium. | Sulphur. | Phosphorus. | |
|---|---|---|---|---|
| 1. | 3 21 | ·014 | 1·806 | Foundry. |
| 5. | 2·67 | ·081 | 1·853 | Forge. |

It will be seen that the residues from the silica in Table I. are very much less than those in Table II. In Table I. the small amount of residue was chiefly phosphate of iron, due to the oxidation of a small amount of phosphide of iron, which is universally left undissolved by the acid, together with the silica. The residues in Table II. were nearly white; they were fused with bisulphate of potash; complete solution took place. On dissolving, however, in cold water, a gelatinous precipitate was left; this was filtered off, and the clear solution on boiling gave a precipitate, which was at the time considered to be titanic acid.

In preparing my recent paper referred to above, the pig used in Table II. was again examined: it was soon found, however, that the residue from the silica was not titanic acid, although in the interim between my first and second examination, samples of this pig were examined by a friend of mine, and by one of my pupils, both of whom found titanium in the pig, evidently mistaking vanadium for titanium, as will presently be shown.

The method found to be the most advantageous in separating the vanadium from the pig, was the same as that employed to separate titanium, viz., by dissolving the borings in dilute hydrochloric acid, and after the pig was nearly all dissolved, adding some strong acid, and boiling well; the chloride of iron was then filtered off from the graphite and silica, the filter well washed from chloride of iron, and treated with a dilute solution of potash to dissolve the silica; the potash thoroughly washed out; and the filter treated with hydrochloric acid, washed until all the acid was removed, then dried, ignited, and burnt over a Bunsen's burner, or better in a muffle. The residue left was a semi-fused mass, apparently consisting of a mixture of a fusible and infusible oxide, staining a porcelain crucible yellow, and adhering strongly to it, some portions of the mass being of a purply blue colour, similar to the bloom on a plum.

The following are the residues obtained from different samples of pig from the two above mentioned localities. It will, however, be seen that the pig from Seend contains less than half that contained in the Westbury pig.

TABLE V.

*Westbury Pig Iron* (1860) (*Grey*), *No.* 1, *best Foundry.*

| | Grains taken. | Gave residue. | Residue per cent. |
|---|---|---|---|
| A. | 127·325 | ·99 | ·777 |
| B. | 1066·72 | 8·60 | ·866 |
| C. | 246·81 | 2·19 | ·887 |

Sample C was dissolved in dilute commercial sulphuric acid; the residue contained a little iron.

*Westbury Pig* (*Grey*), *No.* 5 *Forge Pig.*

| | Grains taken. | Gave residue. | Residue per cent. |
|---|---|---|---|
| C′. | 236·11 | 2·04 | ·864 |

*Westbury Pig,* 1863, *No.* 1, *best Foundry.*

| | Grains taken. | Gave residue. | Residue per cent. |
|---|---|---|---|
| D. | 231·25 | 2·088 | ·901 |
| E. | 230·455 | 1·935 | ·839 |

*Westbury White Pig,* 1863.

| Grains taken. | Gave residue. | |
|---|---|---|
| 231·655 | 8·200 | Residue contained a large quantity of oxide of iron. |
| 134·81 | 3·435 | |

*Seend Pig, No.* 1, *best Foundry,* 1860.

| Grains taken. | gave residue. | Residue per cent. |
|---|---|---|
| 518·4 | 1·82 | ·351 |

The semi-fused residue treated with concentrated hydrochloric acid, gave off chlorine, and formed a brownish-yellow solution, which, on boiling, soon became of a beautiful green colour, some amount of a black insoluble residue remaining undissolved in the form of a fine powder. On adding nitric acid, no perceptible change took place, and the heavy black residue did not appear to be at all affected by it. The residue was separated from the black insoluble matter, the soluble portion was evaporated on the water-bath, and the greater part of the free acid evaporated: a syrupy, dark-greenish mass was then left, the sides of the dish being of a brownish colour. On adding water to this, a beautiful blue solution was formed, and a small amount of a white, insoluble, flocculent matter was observed. The solution was green when acid, but blue when free from much excess of acid, or largely diluted with water. On testing this solution, it gave all the characteristic reactions of vanadium-salts, the most marked being the yellow precipitate with ferrocyanide of potassium, which, on standing, acquires a greenish tinge. From the above reaction no iron can be present in the residue. It may be stated that, in the examination of several samples of pig, the graphite has been obtained nearly pure, or mixed with some of the rarer metals occasionally occurring in pig-iron, the oxides of which may be obtained on burning the graphite. For the description of a residue of nearly pure titanic acid in pig-iron, see the Society's Journal before alluded to, vol. xvi, Table I, page 392.

*Examination of the Black Insoluble Matter.*—On fusing the substance with bisulphate of potash, complete solution took place; the fused mass, after cooling, dissolved completely in cold water. The solution, heated to the boiling point, gave an immediate precipitate, which settled down as a dense yellowish-white powder. This precipitate was partially soluble in hydrochloric acid, or, if hydrochloric acid were added before boiling the solution, no precipitation took place, thus showing that it was not titanic acid. The solution, before boiling, gave the distinct yellow coloration with yellow prussiate of potash peculiar to vanadium salts, although a distinct precipitate was not formed until the solution had stood some time.

This black powder is, most probably, suboxide of vanadium; it does not appear to be oxidised, certainly not to any extent, by fuming nitric acid, and appears to be indifferent to acids generally. The precipitate formed on boiling the solution in bisulphate of potash, is a basic sulphate of vanadium. In the various residues obtained from the different samples of pig, the amount of this black residue appeared to be always about in the same quantity. Two determinations were made of the relative quantity of the black oxide, and the results bear out the above conclusion. A portion of residue B (see Table) was weighed out.

| | |
|---|---|
| Residue B, 3·49 grains, gave black oxide ...... | 1·99 |
| Residue E, 2·085 grains, gave black oxide...... | 1·105 |

By proportion 3·49 : 1·99 : : 2·085 : 1·19

The results approximate very closely. It would appear that the amount of residue in the various samples of the same pig, made at different times, is the same in amount, and also in composition. This will be seen on examining Table 5. A and B may be taken as identical in the same pig C, containing a little iron. C′, quite a different quality of pig, made about the same time as the previous sample, agrees in percentage of residue very closely; D is a trifle higher, and E about the same. It must, however, be observed, that in treating the residue from the pig, insoluble in acids, a second time with hydrochloric acid, after having removed the silica by potash, the acid acquires a darkish brown colour; and if the iron it contains be separated by caustic potash, and the filtrate from the iron be acidified with acetic acid, a distinct yellow coloration is obtained with yellow prussiate of potash, thus showing that a small amount of vanadium is dissolved. In experiment E, the substance was treated twice with potash and hydrochloric acid; this may account for the result being a little lower than D. It was also observed, that if, on dissolving the pig in acid, the clear chloride of iron be poured off, and the insoluble portion boiled for a long time with strong hydrochloric acid, this second portion, on filtering, gave a filtrate which differed in colour from the bright green of protochloride of iron, and was tinged brown; this is most probably due to the solution of a little vanadium. As this pig (Westbury) contained so high a percentage of phosphorus, it was thought advisable to test the residue for phosphoric acid. A determination of this acid was made in residue E. The portion soluble in hydrochloric acid was mixed with chloride of ammonium, tartaric acid, ammonia, and chloride of magnesium, and the solution allowed to stand two days. The ammonia-phosphate separated, dried, ignited, and weighed, gave of pyrophosphate of magnesia ·265, corresponding to ·17 $PO_5$; the filtrate from the ammonia-phosphate, gave no indications of the presence of iron with yellow prussiate of potash, or with sulphide of ammonium.

The total residue 2·085 diminished by ·17 $PO_5$ leaves 1·915; hence, assuming that the portion of this residue soluble in acids is vanadic acid, $VO_3$, and that the black residue is suboxide VO, we find for the quantity of vanadic acid,

$$1{\cdot}915 - \overset{VO.}{1{\cdot}105} = \overset{VO_3.}{{\cdot}81}$$

Consequently, the equivalent of vanadium being 68·6, the percentage of metal will be—

$$\left.\begin{array}{ccccccc} VO. & & V. & & VO. & & V. \\ 76{\cdot}6 & : & 68{\cdot}6 & :: & 1{\cdot}105 & : & 989 \\ VO_3. & & & & VO_3. & & \\ 92{\cdot}6 & : & 68{\cdot}6 & :: & {\cdot}81 & : & 60 \end{array}\right\} = 1{\cdot}589.$$

$$\begin{array}{ccccccc} Pig. & & V. & & & & V. \\ 231{\cdot}25 & : & 1{\cdot}589 & :: & 100 & : & 686. \end{array}$$

Two trials were made to endeavour to obtain vanadium from white pig; it was, however, found impossible to separate the iron completely. As in the case of the other pig, the residue obtained in the first experiment was treated similarly to the grey pig; in the second, the residue, after dissolving out the iron in dilute acid, was boiled with concentrated acid for some time, and after filtering off the insoluble matter, was treated twice with potash and hydrochloric acid alternately, to see if the iron could not be dissolved out; it was, however, as is seen by the result, unsatisfactory; had it been possible to separate the vanadium from the white pig, it would have been far more advantageous, as the grey pig leaves a considerable amount of graphite, which requires much time to burn.

2lbs. of the pulverised pig were operated on with dilute sulphuric acid, the silica being dissolved with potash; the residue obtained by burning the graphite contains, however, some amount of iron. A little vanadic acid was prepared from this by treating the pulverised residue with ammonia, allowing it to stand some time, then gently warming it: the ammoniacal solution was of a deep red colour; this, when evaporated and allowed to stand, deposited a considerable amount of oxide of iron, and small distinct granular crystals attached themselves to the beaker. The solution filtered from oxide of iron was colourless; on evaporating it to dryness and heating it, the vanadic acid separated, first of a beautiful orange-red colour, then green; and on heating more strongly, it assumed a dirty greyish green colour. If the residue when free from iron is treated with ammonia, a beautiful yellow solution is obtained, which, if it has been heated, deposits, on cooling, small granular crystals of vanadiate of ammonia. The residue from the 2lbs. of pig, after being treated with ammonia, was dissolved in hydrochloric acid, the liquid being boiled for many hours; it was then filtered from the greyish residue, and the solution evaporated, to expel the larger portion of free acid. It then deposited on the sides of the beaker a white, amorphous, light substance, which adhered strongly to the glass. This has not yet been examined; it appears to be insoluble in hydrochloric acid. Nitric acid was added to expel the hydrochloric, the larger portion of the free acid driven off, and the solution then treated with ammonia, which threw down an abundant precipitate of oxide of iron. The filtrate, however, contained only a trace of vanadic acid, the whole being precipitated by the ammonia with the iron.

The ore has not yet been tested for vanadium. The following is the analysis of the Seend ores, made by me some time since:—

| Seend Iron Ore. | | Metallic Iron. |
|---|---|---|
| Silica .. .. .. | 18·02 | |
| Peroxide of iron .. | 64·61 | |
| Alumina .. .. | 3·85 | |
| Lime .. .. .. | ·64 | |
| Magnesia .. .. | ·20 | 45·22 |
| Phosphoric acid .. | ·64 | |
| Combined water .. | 10·21 | |
| Moisture .. .. | 1·64 | |
| | 99·81 | |

An account of the analyses of the Westbury ore will be found in the Journal of the Society, vol. xv, page 334. Some remarks are made respecting the oxide of iron obtained, the weight of which could not be made to correspond with the results obtained by standard solution. Now that vanadium has been found in the pig, it is most probable that some vanadic acid is contained in the oxide of iron; the author proposes, however, to re-examine the ore, and lay the result before the Society at some future time. This pig iron will readily furnish any quantity of the hitherto somewhat rare metal vanadium, with tolerable facility. Vanadium is, however, now obtained as a waste product from bauxite, in the manufacture of aluminium, to what extent the author cannot say, or whether it would be a better source for the metal than the pig-iron.

This pig-iron appears to contain more vanadium than that made from the Taberg ore, in Sweden; and, so far as the author is aware, it affords the first instance in which this metal has been found in English pig-iron; some mention is made of its occurrence in a Staffordshire slag (Chem. Gaz. 1848, page 298), by **Dick**, but only a mere notice is given of it.

At the present time, a large quantity of the pig, about 17lbs. is being dissolved in acid, and in a short time the author hopes to lay some further results before the Society, as to the state in which the vanadium occurs in the ore, and the influence it has upon the iron.

## III.—*On a new Reaction for the production of the Zinc-compounds of the Alcohol-radicles.*

By Prof. E. Frankland, F.R.S., and B. F. Duppa, Esq.

In a former communication* we described a new process, by which the mercury-compounds of the alcohol-radicles can be produced in large quantity and with great facility. Having these substances thus at command, it became interesting to ascertain the possibility of transforming them into the corresponding zinc-compounds, by the following reaction:—

$$Hg''\left\{\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}\right. + Zn''_2 = Zn''\left\{\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}\right. + Zn''Hg''$$

Some preliminary experiments completely established the feasibility of the transformation expressed in this equation. It was found that an excess of zinc added to the mercurial compound, readily reacted at a temperature which varied from 100° C. to 130°, eliminating the whole of the mercury, and producing the corresponding zinc compound. This reaction becomes of considerable interest when it is remembered that the processes hitherto devised for the production of organo-zinc compounds in a state of purity, are, as regards those containing amyl and methyl, attended with formidable difficulties, so much so, that the amyl compound has never hitherto been isolated, whilst the methyl body has only been prepared pure in very small quantity, and by processes which are either uncertain or tedious.

---

* Journal of the Chem. Soc. [2], i, p. 415.

### *Action of Zinc upon Mercuric methide.*

Finely granulated and dry zinc is placed in a glass tube strong enough to resist a pressure of about 5 atmospheres, and enough of the mercuric-methide added, to take up about half of the space occupied by the zinc. The tube is next drawn out to a point and laid nearly horizontally in an oil-bath heated to a temperature of 120° C. The object of placing the tube in this position, is to offer a larger surface of contact, so as to hasten the completion of the reaction. After digestion has continued for about 24 hours, the action may be regarded as complete, and the zinc-methide in the tube distilled off. It is, however, advisable to test the liquid from time to time, to ascertain whether the whole of the mercury has been precipitated or not.

On rectification, the zinc-methyl thus obtained boiled constantly at 46° C., and possessed a specific gravity in the liquid state of 1·386 at 10·5° C. An estimation of zinc yielded the following result:—

·2131 grm. was volatilised in a current of carbonic acid, and passed into dilute hydrochloric acid; the chloride of zinc was then precipitated boiling by carbonate of soda, washed, dried, and ignited. It yielded ·1830 grm. oxide of zinc.

These numbers agree closely with the formula—

$$Zn''\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

as seen from the following comparison:—

| | Calculated. | | Found. |
|---|---|---|---|
| $C_2$ …….. | 24 | 25·25 | —— |
| $H_6$ …….. | 6 | 6·31 | —— |
| Zn…….. | 65 | 68·44 | 68·13 |
| | 95 | 100·00 | |

The production of zinc-methyl from mercuric methide by zinc may be represented as follows:—

$$\underbrace{Hg''\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.}_{\text{Mercuric methide.}} + Zn''_2 = \underbrace{Zn''\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.}_{\text{Zinc-methyl.}} + Hg''Zn''.$$

The low boiling point of zinc-methyl naturally precludes the use of glass vessels for its production in large quantities, and it is therefore necessary to resort to the use of an iron digester, similar in construction to the copper one previously described by one of us,* when more than a few ounces of the body are required.

### *Action of Zinc upon Mercuric ethide.*

Mercuric ethide is much more readily acted upon by zinc than the corresponding methyl-compound, a temperature of 100° C. continued for 36 hours being amply sufficient to transform the whole of the mercuric ethide into zinc-ethyl. The reaction is best conducted in the following manner:—The body of a non-tubulated retort being filled with finely granulated zinc, mercuric ethide is then introduced in sufficient quantity to occupy rather more than half the space taken up by the zinc. The neck of the retort may now be closed with a cork; but in order to avoid oxidation during the digestion, it is advisable to draw the neck out in the blow-pipe flame; it is then placed in a steam-bath until the included air is sufficiently expanded, and the point is sealed up. The retort is allowed to remain in the bath, with its neck inclining upwards, for a sufficient length of time. No pressure is generated in this operation; on the contrary, rarefaction, to a small extent, takes place, owing to the oxygen of the contained air being absorbed.

It is easy to judge how the reaction is progressing, by the amount of fluid amalgam which collects at the bottom of the retort; but it is also necessary, as in the process for zinc-methyl, to open the retort once or twice, and to test for mercury in the ethereal liquid, which is readily done by placing a drop of the latter on a watch-glass and breathing upon it, when, after a few moments, the peculiar odour of the mercury-compound will become manifest, if traces of it are still present. As soon as the whole has been decomposed, it is only necessary to submit the contents of the retort to distillation. The distillate boils constantly at 118° C., and exhibits all the properties of pure zinc-ethyl.

The formation of zinc-ethyl by the action of zinc upon mercuric ethide may be thus expressed:—

$$\underbrace{Hg''\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + 2Zn'' = \underbrace{Zn''\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.}_{\text{Zinc ethyl.}} + Hg''Zn''$$

---

* Phil. Trans., 1855, pp. 260 and 261.

In forming an opinion of the comparative value of this and the previously known processes for the production of zinc-ethyl, it must be borne in mind that mercuric ethide is most readily obtained in nearly the quantity indicated by theory, and that this body, in its turn, is completely transformed without loss into zinc-ethyl. On the other hand, the production of the latter by the action of zinc upon iodide of ethyl, involves considerable loss, owing to the intermediate formation of ethiodide of zinc, $Zn\left\{\begin{matrix}C_2H_5\\I\end{matrix}\right.$. This compound not only requires a very high temperature for its decomposition, but also deposits, at the expense of the resulting zinc-ethyl, a considerable quantity of metallic zinc. Nevertheless, we are of opinion that the process we are now proposing is only to to be recommended in the absence of the apparatus necessary for the production of zinc-ethyl by the method first described by one of us.[*] In our hands the processes devised by Pebal[†] and by Rieth and Beilstein[‡] have not given satisfactory results. That of the latter chemists, which appears to be by far the better of the two, yielded us only 40 per cent. of the theoretical quantity, which is greatly below the amount obtained by the use of a metallic digester.

### *Action of Zinc upon Mercuric Amylide.*

Mercuric amylide, treated with zinc in the same manner as mercuric ethide, and exposed in an oil-bath to a temperature of 130°C. for 36 hours, is completely converted into zinc-amyl, which then only requires to be separated from the zinc-amalgam by distillation. On rectification, the distillate began to boil at about 50°C., when a very small quantity of a mixture of amylene and hydride of amyl distilled, whilst the thermometer was rapidly rising to 220°C., between which temperature and 222°C. the remainder of the product passed over.

Submitted to analysis this liquid gave the following results:—

I. ·3214 grm. burnt with oxide of copper, gave ·6834 grm. carbonic acid and ·3112 grm. water.

II. ·3898 grm. gave ·8251 grm. carbonic acid and ·3770 grm. water.

III. ·4815 grm., decomposed by dilute hydrochloric acid, and precipitated with carbonate of soda, gave ·1840 grm. oxide of zinc.

---

[*] Phil. Trans., 1855, p. 259.

[†] Ann. Ch. Pharm. cxviii, 22.

[‡] Ann. Ch. Pharm. cxxvi, 2, 48.

IV. ·6770 grm., decomposed by alcoholic solution of hydrochloric acid, and precipitated as before, gave ·2664 grm. oxide of zinc.

These numbers correspond closely with the formula

$$Zn''\left\{\begin{array}{l}C_5H_{11}\\C_5H_{11}\end{array}\right.$$

as seen from the following calculation :—

| | | | I. | II. | III. | IV. | Mean. |
|---|---|---|---|---|---|---|---|
| $C_{10}$ | 120 | 57·97 | 57·99 | 57·77 | .. | .. | 57·88 |
| $H_{22}$ | 22 | 10·63 | 10·76 | 10·75 | .. | .. | 10·76 |
| Zn | 65 | 31·40 | .. | .. | 30·67 | 31·34 | 31·01 |
| | 207 | 100·00 | | | | | 99·65 |

The action of zinc upon mercuric amylide may therefore be thus represented :—

$$\underbrace{Hg''\left\{\begin{array}{l}C_5H_{11}\\C_5H_{11}\end{array}\right.}_{\text{Mercuric amylide.}} + Zn''_2 = \underbrace{Zn''\left\{\begin{array}{l}C_5H_{11}\\C_5H_{11}\end{array}\right.}_{\text{Zinc-amyl.}} + Hg''Zn''$$

Zinc-amyl is a colourless, transparent and mobile liquid, possessing an amylic odour, and having a specific gravity of 1·022 at 0°C. It boils at 220°C., and distils unchanged. A determinaion of the vapour-density by Gay Lussac's method gave the ollowing numbers :—

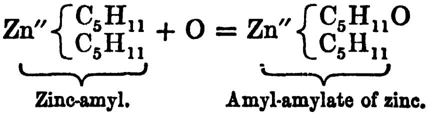
| | |
|---|---|
| Weight of zinc-amyl used | ·3197 grm. |
| Observed volume of vapour | 68·19 c. c. |
| Temperature | 235°C. |
| Height of column of oil | 75·5 mm. |
| Height of inner column of mercury | 142·5 mm. |
| Height of barometer | 755·0 mm. |
| Corrected volume of vapour at 0° C. and 760° mm. pressure | 35·5 c.c. |
| Specific gravity of vapour | 6·95 |

Zinc-amyl vapour, therefore, consists of one volume of zinc vapour united with two volumes of amyl, the whole being condensed to two volumes :—

| | |
|---|---|
| 2 volumes of amyl vapour .......... | 9·8124 |
| 1 volume of zinc vapour .......... | 4·4942 |
| 2 | 14·3066 |
| | 7·1533 |
| Found by experiment.............. | 6·95 |

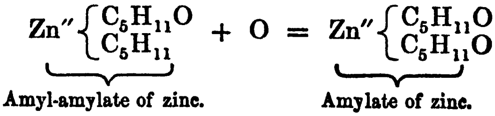
At about 240°C. zinc-amyl slowly decomposes ; a vapour-density taken at this temperature gave the number 6·64, and when the apparatus cooled, it was found that a notable quantity of amylene and hydride of amyl had been formed.

Zinc-amyl fumes strongly when exposed to the air, but it does not ignite spontaneously, as is the case with the corresponding methyl and ethyl compounds ; when dropped into pure oxygen, however, it bursts into brilliant white flame, attended with slight explosion. By slow oxidation, zinc-amyl is first converted into *amyl-amylate of zinc :*



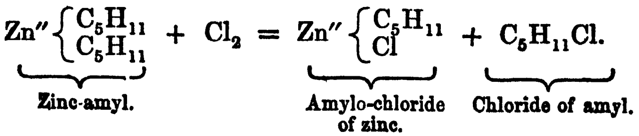
$$\underbrace{Zn''\left\{\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\right.}_{\text{Zinc-amyl.}} + O = \underbrace{Zn''\left\{\begin{matrix}C_5H_{11}O\\C_5H_{11}\end{matrix}\right.}_{\text{Amyl-amylate of zinc.}}$$

and, finally, into *amylate of zinc :*



$$\underbrace{Zn''\left\{\begin{matrix}C_5H_{11}O\\C_5H_{11}\end{matrix}\right.}_{\text{Amyl-amylate of zinc.}} + O = \underbrace{Zn''\left\{\begin{matrix}C_5H_{11}O\\C_5H_{11}O\end{matrix}\right.}_{\text{Amylate of zinc.}}$$

When zinc-amyl is brought into contact with chlorine, it inflames spontaneously, burning with a lurid flame, which deposits much soot. A more gradual action would doubtless be attended with the formation of *amylo-chloride of zinc* and chloride of amyl :



$$\underbrace{Zn''\left\{\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\right.}_{\text{Zinc-amyl.}} + Cl_2 = \underbrace{Zn''\left\{\begin{matrix}C_5H_{11}\\Cl\end{matrix}\right.}_{\text{Amylo-chloride of zinc.}} + \underbrace{C_5H_{11}Cl.}_{\text{Chloride of amyl.}}$$

and, secondly, of chloride of zinc and chloride of amyl:

$$\underbrace{\mathrm{Zn}''\left\{\begin{matrix}\mathrm{C_5H_{11}}\\ \mathrm{Cl}\end{matrix}\right.}_{\text{Amylo-chloride of zinc.}} + \mathrm{Cl_2} = \underbrace{\mathrm{Zn}''\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.}_{\text{Chloride of zinc.}} + \underbrace{\mathrm{C_5H_{11}Cl}}_{\text{Chloride of amyl.}}.$$

The addition of iodine to zinc-amyl is attended with considerable elevation of temperature, the materials becoming pasty, from the formation of *amylo-iodide of zinc*:

$$\underbrace{\mathrm{Zn}''\left\{\begin{matrix}\mathrm{C_5H_{11}}\\ \mathrm{C_5H_{11}}\end{matrix}\right.}_{\text{Zinc-amyl.}} + \mathrm{I_2} = \underbrace{\mathrm{Zn}\left\{\begin{matrix}\mathrm{C_5H_{11}}\\ \mathrm{I}\end{matrix}\right.}_{\text{Amyloiodide of zinc.}} + \mathrm{C_5H_{11}I}$$

The further addition of iodine rendered the materials again fluid, and almost limpid, owing to the decomposition of the amylo-iodide of zinc:

$$\underset{\text{Amylo-iodide of zinc.}}{\underline{\mathrm{Zn}''\left\{\begin{matrix}\mathrm{C_5H_{11}}\\ \mathrm{I}\end{matrix}\right.}} + \mathrm{I_2} = \underbrace{\mathrm{Zn}''\left\{\begin{matrix}\mathrm{I}\\ \mathrm{I}\end{matrix}\right.}_{\text{Iodide of zinc.}} + \underbrace{\mathrm{C_5H_{11}I}}_{\text{Iodide of amyl.}}.$$

On treating the product with water, iodide of zinc dissolved, whilst a heavy liquid, boiling at 147° C. and having the properties of iodide of amyl, subsided to the bottom of the vessel.

### *Action of various Metals on Mercuric ethide.*

From the readiness with which the mercurial compounds of the alcohol-radicles are decomposed by zinc, we were induced to test their behaviour with other metals. For this purpose, we selected mercuric ethide, since we found this compound to be more readily acted upon by zinc than the corresponding methyl and amyl bodies.

*Iron*, reduced from the sesquioxide by hydrogen, was submitted to the action of mercuric ethide, at temperatures varying from 100° to 150° C., but with no other result than the formation of large quantities of inflammable gas, and the precipitation of mercury without amalgamation, no traces of a ferrous or ferric compound of ethyl being formed. There can be little doubt that the mercuric ethide was gradually decomposed by a lengthened exposure to a high temperature, quite independently of any action of the iron, which, indeed, appeared to be null.

*Copper*, in the state of filings, was treated with mercuric ethide for three hours at 100° C., without any effect being produced, but after exposure for five or six hours to 150° C., the metal became slightly amalgamated, and gas was evolved when the tube was opened. In this case, the precipitation of mercury appears to have arisen, rather from the decomposition of the ethide by heat, than from any action of the metallic copper upon that body.

*Cadmium* and mercuric ethide react upon each other but very slowly and imperfectly. As in the reaction with zinc, amalgam is formed, and also a considerable quantity of cadmium-ethyl; but notwithstanding long digestion at a temperature varying from 100° to 130° C., we were unable to obtain a product free from the mercury compound.

Finely powdered *bismuth* heated with mercuric ethide, was acted on to a considerable extent, bismuth-ethyl being formed in large quantity; nevertheless, though the digestion was continued for many hours, at temperatures varying from 120° to 140° C., we were unable to decompose the whole of the mercuric body. Had a larger proportion of bismuth been used, so as to present a greater surface of contact, the conversion would probably have been perfect; but as our object was merely to point out the behaviour of the various metals with mercuric ethide, we did not pursue this reaction further, although we consider that it promises to produce organo-compounds of bismuth with great facility.

*Silver* does not decompose mercuric ethide at 100° C., although at 150°, considerable action takes place, gas in large quantities being evolved; but no trace of an argentiferous organic compound is perceptible.

*Gold leaves* placed in mercuric ethide heated to 120° C., rapidly dissappear, forming a perfect amalgam, accompanied by a liberation of gas. No organo-auric body is, however, formed.

# IV.—*On the Synthesis of Organic Substances.*

### By M. Berthelot.

[A Discourse delivered before the Chemical Society of London, June 4th, 1868.]*

Analysis shows that the generality of organic substances are formed: some, of the two elements, carbon and hydrogen; others of three elements, viz., carbon, hydrogen, and either oxygen or nitrogen; others, again, of the four elements, carbon, hydrogen, oxygen, and nitrogen. These four elements, united in extremely varied proportions, constitute the proximate principles of the liquids and tissues of the animal and vegetable body. Hence it is these four elements that we have to combine, two and two, three and three, four and four, in order to effect the synthesis of organic substances. And the necessity of this undertaking is obvious; since it furnishes the only rigorous proof that we can obtain of the identity of the forces which regulate the chemical phenomena of organic, with those which govern the same phenomena in mineral substances.

I shall endeavour to show how, by starting from the elements, and from mineral compounds, we can combine carbon, step by step, first with hydrogen, then with oxygen, and lastly with nitrogen, thereby producing organic compounds, some identical with certain natural bodies, others only analogous thereto, but at the same time serving as starting points for the formation of new natural bodies.

Instead of explaining the general methods of effecting this object, the development of which would lead us too far, I will take a series of particular examples, borrowed, for the most part, from my own experiments.

And first, let us take the elements as our point of departure:—

Carbon and hydrogen are capable of uniting directly. It is sufficient to bring the carbon to a state of incandescence by the electric arc, and cause a stream of hydrogen to pass between the poles. The hydrogen then immediately enters into combination with the carbon, giving rise to a gaseous hydrocarbon called acetylene:

$$C_4 + H_2 = C_4H_2.$$

The experiment is performed in a glass globe, having two tubulures opposite to one another. Through one of these tubulures is inserted the positive pole of a voltaic battery, together with the tube which conveys the hydrogen; through the other are introduced the negative pole of the battery, and a tube by which the hydrogen passes off.

---

* Translated by the Editor.

The two poles of the battery are terminated by pieces of the charcoal from gas-retorts; they can be pushed forwards or backwards within the globe; and are in connection with a Bunsen's battery of from 40 to 90 pairs. The essential condition of success is the production of the voltaic arc; the brighter it is, the greater will be the quantity of acetylene obtained. Before bringing the poles together, a current of hydrogen is passed through the globe for about a quarter of an hour, in order to drive out the air. The poles are then brought together, the arc shoots forth, and the production of acetylene immediately commences, continuing as long as the arc is maintained. About half the carbon lost by the poles is converted into acetylene, the rest being dispersed in the form of fine dust, which collects on the inner surface of the globe.

To afford ocular demonstration of the formation of acetylene, it is sufficient to pass the gas which issues from the globe into a bottle containing an ammoniacal solution of cuprous chloride. This reagent absorbs the acetylene, giving rise to cuprous acetylene, $C_4Cu_2H$, a compound distinguished by its insolubility and its brick-red colour.

From this cuprous acetylene it is easy to obtain acetylene itself in the pure state, by the action of warm hydrochloric acid. Acetylene is then evolved, and cuprous chloride produced :

$$C_4Cu_2H + HCl = C_4H_2 + Cu_2Cl.$$

Acetylene is, as you observe, a colourless gas, which burns with a very smoky flame. It is a very important gas, being invariably produced when organic substances are heated to redness. It is a constituent of coal-gas, to which it communicates its rather fetid odour and illuminating power.

We have thus succeeded in effecting the direct combination of carbon and hydrogen, in the form of acetylene.

Acetylene furnishes a starting point for the formation of other products. We shall, in the first place, change it into a new hydrocarbon, viz., olefiant gas or ethylene, a compound which has been known for a long time, and will serve for new experiments.

To transform acetylene into olefiant gas, it is sufficient to fix upon the acetylene two equivalents of hydrogen:

$$C_4H_2 + H_2 = C_4H_4.$$

This hydrogenation is easily effected by treating cuprous acetylene with hydrogen. The hydrogen must, however, be generated, not in an acid solution, which would attack the acetylene, but in an alkaline liquid, which has no action on that compound. I avail myself, for the purpose, of the action of ammonia upon zinc. By this means, the acetylene is transformed into olefiant gas.

From olefiant gas we shall be able to produce new compounds. For example, it may be transformed into alcohol, by combination with the elements of water. To produce this result, let us take olefiant gas, and agitate it with strong sulphuric acid. This agitation, to be effectual, must not be like ordinary agitations. To bring about the absorption of a litre of olefiant gas by sulphuric acid, requires 3,000 shakes, and more than half an hour's time. For the absorption of 30 litres, we should require from 50,000 to 60,000 agitations. Under these conditions, the gas is gradually absorbed, and unites directly with the sulphuric acid. Let us now take the compound so produced, add to it 8 or 10 volumes of water, and distil; we shall then obtain alcohol, that is to say, the hydrate of olefiant gas. In short, our experiment reduces itself to a hydration:

$$C_4H_4 + H_2O_2 = C_4H_6O_2.$$

We have thus formed the first compound, which may be called natural, namely, alcohol, that is to say, a ternary compound, containing carbon, hydrogen, and oxygen. We have succeeded in causing these elements to unite successively, and have thus arrived at one of the most important of organic compounds—one of the starting points of those organic series, which are so rich in metamorphoses. Given the indefinitely extended chain of these compounds, we have succeeded in forging the first links by methods belonging purely to mineral chemistry.

Before proceeding further, it is necessary to show how the same result may be obtained by another method, somewhat longer, but not less fertile in results. It proceeds experimentally, no longer from the uncombined elements, but from elements completely oxidised in the state in which they are found in nature, namely, in that of water and carbonic acid.

Given then water and carbonic acid, how are we to produce organic substances from them? Such is the problem which we are about to attack, not by theories more or less controvertible, but by direct and effective experiments. To render clearer the mode of solving this problem, I will, before attempting its solution in the case of oxygen-compounds, such as water, $H_2O_2$, and carbonic acid, $C_2O_4$, proceed to solve it with the corresponding sulphur-compounds, viz., sulphuretted hydrogen $H_2S_2$, and sulphide of carbon $C_2S_4$, with which the result is more easily obtained.

It is sufficient, indeed, to subject these two compounds to the action of a substance capable of removing the sulphur which they contain. The hydrogen and carbon are then set free, and being brought together in the nascent state, unite and form a hydrocarbon analogous in composition to sulphide of carbon, namely, marsh-gas, $C_2H_4$.

The removal of the sulphur from sulphuretted hydrogen and sulphide of carbon is effected in this manner with the greatest facility; all that is required is to subject the gaseous mixture of these two bodies to the action of a metal, especially copper, at a low red heat:

$$C_2S_4 + 2H_2S_2 + 8Cu = C_2H_4 + 8CuS.$$

The passage from sulphocarbonic acid to marsh-gas, which appears thus simple, is analogous to that from carbonic acid to marsh-gas; only the oxygen is more difficult to separate from the carbon than is the sulphur, and it becomes necessary to effect the transformation in two successive stages, resorting in the end to the highly refined conditions of the nascent state.

We begin by depriving the carbonic acid of half its oxygen, which may be done in all sorts of ways, by the action of hydrogen or of a metal, for example. The carbonic oxide thus obtained is introduced into a combination which alters all its conditions of stability: it is made to combine with the elements of water, producing formic acid:

$$C_2O_2 + H_2O_2 = C_2H_2O_4.$$

This act of combination, viewed with reference to the conditions by which it is determined, is one of the most remarkable in organic chemistry. The carbonic oxide does not indeed unite directly with the elements of water, but the combination may be brought about by the influence of potash, which itself unites with the resulting compound. The reaction is not immediate. Carbonic oxide, placed in contact with potash, is absorbed slowly and gradually, the absorption requiring several months to complete it at ordinary temperatures, and several days even at 100°. The slowness of this reaction is well worthy of remark, showing as it does the influence of time in the chemical phenomena developed in organised beings. Moreover, the reaction under consideration leads to the formation of an acid widely diffused among plants and animals.

We have now got formic acid, that is to say, the hydrate of carbonic oxide. On placing this body under suitable conditions, the elements of water and those of carbonic oxide react upon each other in the nascent state, producing ultimately a more highly oxidised carbon-compound, viz., carbonic acid, and a more highly hydrogenised carbon compound, viz., marsh-gas:

$$4C_2H_2O_4 = 3C_2O_4 + C_2H_4 + 2H_2O_2.$$

This is the most frequent of all the modes of partition occurring in organic chemistry, being exemplified in the formation of benzol at the expense of benzoic acid; of acetone, at the expense of acetic acid, &c., &c.

To determine this partition, it is not sufficient to expose free formic acid to the action of heat, which would simply reproduce water and carbonic oxide; but it is necessary to call in the aid of a body capable of uniting with carbonic acid. For this purpose I have had recourse to baryta, using the formate of baryta, without excess of base, in order not to decompose the water itself. In short, formate of baryta is decomposed by distillation, yielding marsh-gas:

$$4C_2HBaO_4 = C_2H_4 + C_2O_4 + 2(C_2O_4.Ba_2O_2).$$

This formula exhibits the simplicity of the reaction even better than the preceding.

To resume. You perceive that we have started from water and carbonic acid. A first reduction, effected by free hydrogen, has robbed the carbonic acid of half its oxygen, converting it into carbonic oxide; and a second reduction, brought about by nascent hydrogen derived from the elements of water, has, in its turn, transformed the carbonic oxide into a hydrocarbon.

The transformation of carbonic acid, $C_2O_4$, into marsh-gas is, therefore, by the play of affinities which concur in producing it, essentially analogous to that of sulphide of carbon, $C_2S_4$, into marsh-gas.

Let us now direct our attention to marsh-gas, the hydrocarbon that we have just obtained, and see by what means we can transform it into an oxygenated compound, in particular into an alcohol. This transformation is effected in two stages: 1. When marsh-gas is mixed with an equal volume of chlorine, and the mixture exposed to diffused daylight, under conditions which I have elsewhere specified, we obtain, by substitution, methylchlorhydric ether:

$$C_2H_4 + Cl_2 = C_2H_3Cl + HCl.$$

2. This ether, decomposed by potash, yields methylic alcohol $C_2H_4O_2$:

$$C_2H_3Cl + KO,HO = C_2H_4O_2 + KCl.$$

We have thus a new alcohol corresponding to marsh-gas, in the same manner that common alcohol, obtained as above described, corresponds to olefiant gas, except that the methylic alcohol has resulted from the addition of oxygen to marsh-gas:

$$C_2H_4 + O_2 = C_2H_4O_2;$$

whereas the common alcohol resulted from the addition of water to olefiant gas:

$$C_4H_4 + H_2O_2 = C_4H_6O_2.$$

The formation of these two alcohols represents two distinct and general modes of formation, the one applying to all hydrocarbons analogous to marsh-gas, the other to all hydrocarbons analogous to olefiant gas. You see by this how fertile are the methods of synthesis, which I have the honour of explaining to you. In fact, the formation of the hydrocarbons, and of the alcohols, leads to the formation of all other organic compounds. This point is worthy of some further developments, which I am about to lay before you.

1. Given a hydrocarbon, required a direct method of transforming it into hydrocarbons of greater complexity.

2. Given an alcohol obtained by the metamorphosis of a hydrocarbon, to find methods of transforming it into other compounds, containing oxygen, nitrogen, &c.

Let us begin with the first point.

In this case, also, I shall have recourse to examples for the purpose of defining methods, and I shall take them from the history of marsh-gas, that is to say, of the hydrocarbon which we have just produced from water and carbonic acid.

Marsh-gas may be changed into more complicated hydrocarbons by the condensation of several molecules into one. Let us, for example, subject marsh-gas to a very high temperature, or cause a succession of induction-sparks to pass through it, which will produce the same effect. By limiting the action to a certain point, we shall transform the marsh-gas into acetylene, that is to say, a gaseous hydrocarbon containing twice the quantity of carbon in the same volume:

$$2C_2H_4 = C_4H_2 + H_6.$$

Here is the experiment going on. The marsh-gas flows slowly from a gasometer, and passes through a small egg-shaped glass vessel, in the middle of which is an arrangement for causing the induction-spark to pass through it. Beyond the egg-shaped vessel is a bottle filled with an ammonical solution of cuprous chloride, for the purpose of demonstrating the formation of acetylene. On sending a series of induction-sparks through the apparatus, the marsh-gas is decomposed, and the formation of the red precipitate of cuprous acetylene indicates the immediate and abundant production of acetylene. The conversion of marsh-gas into acetylene may likewise be determined by the action of heat alone, without the electric spark. This hydrocarbon, which we had previously obtained by the direct combination of its elements, has now, therefore been produced from marsh-gas, which is itself derived from water and carbonic acid. From acetylene we can, by the action of nascent hydrogen, produce olefiant gas, as I have already shown: hence olefiant gas is derived in a very simple manner from marsh-gas. Moreover, the conversion of marsh-gas into olefiant gas ought to take place, every time that marsh-gas, either free or in the nascent state, is decomposed in presence of nascent hydrogen, at a temperature low enough to allow of the existence of olefiant gas. This conclusion is confirmed by experiment. In the preparation of marsh-gas from sulphide of carbon and sulphuretted hydrogen by the action of copper, the conditions just mentioned are fulfilled, and accordingly a certain quantity of olefiant gas is obtained. This gas is also produced in the decomposition of formate of baryta by heat.

With olefiant gas, derived in this manner from marsh-gas, we can, moreover, produce alcohol, and thus enter into the general series of organic chemistry.

The condensation of marsh-gas may be carried considerably beyond the formation of acetylene, and made to yield naphthalin, that is to say, a hydrocarbon formed by the condensation of ten molecules of marsh-gas into one:

$$10C_2H_4 = C_{20}H_8 + H_{32}.$$

The transformation takes place under the influence of a temperature at once elevated and long continued. We may for example enclose the marsh-gas in a tube of very refractory glass, and keep it for several hours at a temperature as near as possible to that at which Bohemian glass softens.

This same condensation is produced under the influence of the nascent state, at the expense of a small quantity of the marsh-gas prepared from sulphide of carbon.

The formation of still higher hydrocarbons might doubtless be effected by analogous processes; but I refrain from pursuing this part of the subject further, desiring to point out to you other modes of condensing of marsh-gas, brought about by different methods.

Instead of marsh-gas itself, let us take one of its derivatives, namely, bromoform, that is to say, a body, $C_2HBr_3$, in which 3 equivalents of hydrogen in marsh-gas, $C_2H_4$, are replaced by 3 equivalents of bromine. This body contains 2 equivalents of carbon to 1 equivalent of hydrogen, these elements being contained in it in the same proportion as in benzol, $C_{12}H_6$. Now experiment shows that when the bromine contained in bromoform is removed at a high temperature, as by directing the vapour of that compound on red-hot copper, a certain quantity of benzol is obtained, 6 molecules of marsh-gas, or rather of its derivative, being thus condensed into a single molecule:—

$$6C_2H_4 = C_{12}H_6 + H_{18}.$$
$$6C_2HBr_3 + 18Cu = C_{12}H_6 + 18CuBr.$$

This reaction is analogous to the preceding; in either case we remove from marsh-gas a portion of its hydrogen and condense it; only in the one case the two changes are effected at once, whereas in the other they take place by successive stages.

Here is another reaction in which marsh-gas is made to yield a hydrocarbon of greater condensation, by combination with another carbon-compound. Let us cautiously direct a mixture of marsh-gas and carbonic oxide through a tube heated to low redness: a certain quantity of propylene will then be formed:

$$2C_2H_4 + C_2O_2 = C_6H_6 + H_2O_2.$$

In this reaction, the carbon of two molecules of marsh-gas is added to that of one molecule of carbonic oxide.

This reaction may also be invoked to explain the formation of a small quantity of propylene in the distillation of formate of baryta; and it is doubtless to reactions of the same order that we must attribute, on the one hand, the formation of hydrocarbons of still greater complexity, but belonging to the same series, $C_{2n}H_{2n}$, as olefiant gas and propylene, in the distillation of the formate above mentioned—and on the other, the production of this same series of hydrocarbons, which has been experimentally demonstrated, as high as amylene, in the distillation of acetate of soda.

These last phenomena, however, admit of a more natural explanation. In fact, we have just seen that the condensation of marsh-gas in the nascent state is of frequent occurrence, and takes place even more easily with the nascent hydrocarbon than with the same body in the free state. Now, in the distillation of alkaline acetates and analogous salts, the oxygen remaining united with the base in the form of carbonic acid, the carbon and hydrogen are brought together while in the nascent state, and tend to unite in equal numbers of equivalents, so as to produce a very simple hydrocarbon, viz., methylene, $C_2H_2$. But this hydrocarbon has never yet been obtained in the free state. All attempts to isolate it have resulted, either in the formation of quite different, or most frequently of more condensed products. The dry distillation of acetates and analogous salts yields, as experiment shows, a whole series of hydrocarbons, which may be regarded as formed by the condensation of 2, 3, 4, 5, or more molecules of methylene into one. Hence results the formation, known to take place under these conditions, of—

| | | | |
|---|---|---|---|
| Olefiant gas.......... | $C_4H_4$ | or | $(C_2H_2)_2$ |
| Propylene .......... | $C_6H_6$ | or | $(C_2H_2)_3$ |
| Butylene............ | $C_8H_8$ | or | $(C_2H_2)_4$ |
| Amylene............ | $C_{10}H_{10}$ | or | $(C_2H_2)_5$ |

To resume: After having formed certain hydrocarbons, such as acetylene and marsh-gas from their elements, we have called to our aid three distinct methods of obtaining hydrocarbons of a higher degree of condensation, viz. :—

1. The *direct condensation* of a hydrocarbon into one more highly condensed.

| | | |
|---|---|---|
| It is thus that marsh-gas............ | | $C_2H_4$ |
| becomes transformed into | acetylene | $C_4H_2$ |
| ,, ,, | olefiant gas | $C_4H_4$ |
| ,, ,, | benzol | $C_{12}H_6$ |
| ,, ,, | naphthalin | $C_{20}H_8$ |

2. *Simultaneous condensation,* by virtue of which several hydrocarbons, whose formulæ are multiples one of the other, are produced at the same time, *e.g.*, the simultaneous formation, by the distillation of formates and acetates, of—

| | |
|---|---|
| Olefiant gas .............. | $C_4H_4$ |
| Propylene................. | $C_6H_6$ |
| Butylene ................ | $C_8H_8$ |
| Amylene ................ | $C_{10}H_{10}$ |

3. The *union of the two simple molecules* into a more complex molecule.

An instance of this is found in the combination of marsh-gas and carbonic oxide, leading to the formation of propylene, $C_6H_6$.

These three methods are of general application, and it is by varying them according to particular cases, and the conditions of stability of the bodies subjected to experiment, that we can form, from the simplest compounds, products of a higher and higher order, and re-ascend by synthesis the scale of successive decompositions which has been brought to light by analysis.

The application of these methods becomes easier as we ascend to compounds of greater complexity, because these compounds are susceptible of reactions more and more varied and delicate. To produce the first organic bodies from the elements, we are obliged, as it were, to go backwards on the scale of affinities, taking compounds which are very stable and difficult to attack, and transforming them into compounds of much less stability. But these first terms, once obtained, introduce us into the domain of organic chemistry, where reactions take place with greater facility and are easier to manage. In organic synthesis, the first steps, those namely which follow directly after the elements, are the most difficult to mount.

I have now shown by what methods the hydrocarbons may be obtained, either from the elements, or by reciprocal transformation of the hydrocarbons themselves. I have also explained the general methods by which the alcohols may be produced from the hydrocarbons; and, in short, I have demonstrated the complete synthesis of the hydrocarbons and alcohols by means of the elements. This complete synthesis is the foundation of all others: for, the alcohols being once obtained, we can, by regular methods, —the result of experiments made in organic chemistry during the last forty years,—produce organic compounds without number.

By careful oxidation of the alcohols we obtain the aldehydes, a new group of substances, including common aldehyde, the type of all the rest, the essential oils of bitter almonds, cinnamon, and cumin, common camphor, and, in short, the greater number of oxygenated essential oils existing in nature.

By a further degree of oxidation, the aldehydes are, in their turn, transformed, giving rise to organic acids. In this manner may be obtained formic, acetic, butyric, valeric and benzoic acids, belonging to the series of natural monobasic acids, and likewise certain bodies belonging to the group of natural polybasic acids: for example, oxalic acid; succinic acid, which Dr. Maxwell Simpson has lately obtained by a general method; tartaric acid obtained by MM. Perkin and Duppa, &c.

After bodies formed by oxidation, come those which result from the reciprocal union of oxygenated compounds. The combination of alcohols and acids gives rise to the compound ethers which comprise the odoriferous principles of certain fruits, and more especially the natural fats, that is to say, one of the fundamental groups among the constituent principles of organised beings. The synthesis of these principles is thus completely realised.

It was by combining the alcohols one with the other, that Professor Williamson established his theory of etherification, the fertility of which has extended over the entire range of chemistry.

With the alcohols are likewise connected those compound metallic radicles, the study of which is so successfully pursued by Dr. Frankland, and which appears to be destined some day to play an essential part in synthetic researches.

Having now completed the circuit of the combinations formed by carbon, hydrogen, and oxygen, it remains to speak of the formation of compounds containing nitrogen.

All known azotised compounds (I speak of those occurring in nature) are capable of giving off their nitrogen in the form of ammonia. Now, it is by the union of ammonia with binary and ternary carbon-compounds, that we are able at the present day to reproduce a multitude of compounds containing nitrogen.

At the head of these reproductions, must be placed that of urea, by Wöhler, the formation, that is to say, of the most simple of natural alkaline compounds, for it is derived from carbonic acid and ammonia. This discovery, made thirty-five years ago, was the first step in organic synthesis.

It is to Zinin that we are indebted for the first general methods of forming organic alkalis. His process consisted in subjecting a hydrocarbon to the action of nascent ammonia. In this manner he converted benzol into aniline, a discovery which has given rise to the artificial formation of a host of remarkable colouring matters. Wurtz, by a fertile idea, connected the formation of organic alkalis with the union of ammonia and the alcohols. Hofmann has generalised this idea, and has thence arrived at that admirably prolific theory, the consequences of which he follows out day by day with such signal success. It is likewise by the action of ammonia on oxygenised principles, that MM. Perkin and Duppa have produced glycollamine and leucine, two alkalis which play an important part in animal tissues.

But I must pause. A complete survey of the synthetic applications, rendered possible by the complete synthesis of the hydrocarbons and alcohols, would require us to trace the history of the principal discoveries relating to the theory of the alcohols, made during the last thirty years.

To sum up: We now know how to unite carbon with hydrogen, and thus form binary compounds. With these primary hydrocarbons we are able, and by general methods, to form new hydrocarbons of continually increasing condensation, apparently embracing the entire range of organic bodies.

The hydrocarbons being obtained, we can transform them into alcohols.

With the alcohols, we can produce the aldehydes, acids, compound ethers, and mixed ethers, that is to say, the whole range of ternary compounds containing carbon, hydrogen, and oxygen.

Finally, the union of ammonia with the binary and ternary compounds of carbon, completes the solution of the problem, by demonstrating the reproduction of nitrogenised compounds.

It is thus that synthesis proceeds in the reproduction of organic bodies; but this reproduction possesses a peculiar character and a high degree of philosophical importance. In fact, to effect these interesting reproductions, synthesis does not work by chance, but proceeds from a knowledge of those general laws, of which natural beings represent, in a certain sense, the consequences and particular applications.

It is these special cases only that can be made known to us by analysis. But the general law according to which they have been produced, can be known and demonstrated by synthesis alone. Analysis is here a simple but indispensable instrument for conducting us to synthesis, which is the true end of our science.

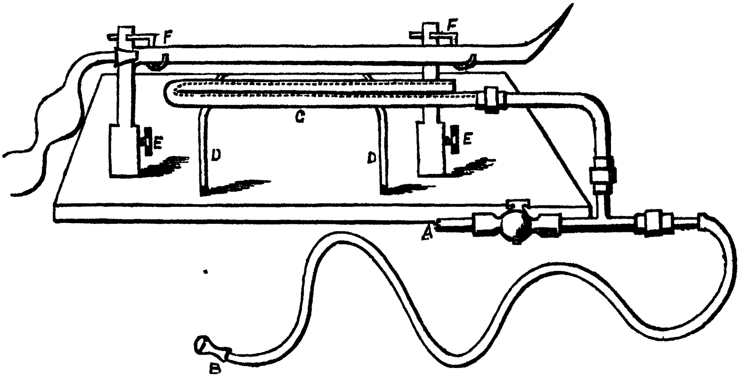
Thus, the fertility of synthesis extends far beyond the mere reproduction of natural compounds. The synthesis of the natural fats, for example, has extended our knowledge of the constitution of those bodies, much beyond that which had been revealed by analysis; it led me, in short, to a new and general theory, that of the polyatomic alcohols, and gave me the means of forming, by virtue of this theory, a multitude of fatty bodies, analogous to the natural fats, but never yet known to occur in nature.

It is thus that synthesis, at the same time that it reproduces the order of natural compounds, likewise calls into existence a new artificial order, more extended, with regard to general ideas, and more fertile in applications, than the natural order itself.

## V.—*On a new Combustion Blowpipe for Organic Analysis.*

By William Herapath, Sen., J.P., F.C.S.

For many years I have been in the habit of using a blowpipe in organic analysis, which I think will render much more easy and prompt the combustions required to determine the ultimate constitution of vegetable and animal matters. It is founded upon the principle of my gas blowpipe, now so common in laboratories and workshops; this principle has also, since my protection, been adopted in the construction of Griffin's and Gore's chemical furnaces.



A is the gas service-pipe attached to the laboratory table.

B is the mouthpiece and elastic tube through which the air or breath is driven to mix with the gas before combustion.

C is the burner, formed of a piece of gas service-tube, bent back upon itself once or twice, about $\frac{1}{4}$ of an inch apart, and having a series of fine holes made in each length, pointing inward.

D, two brackets to support the burner.

E, two pillars of tube with adjusting screws to bear the combustion tube by the wire hooks F.

The use of this burner is very simple. The combustion-tube being filled and arranged, the gas is turned on slightly, but a sheet of thin iron interposed prevents the flame from acting on any part of the tube but that nearest its exit. When it has been gradually heated, a moderate stream of air is sent from the lungs through the gas until that part of the tube is fully red-hot, the iron plate is now slowly drawn backwards until the whole of the tube and contents shall have been made fully red-hot and the combustion completed; then, by moderating the blast and reducing the flow of gas, the tube gradually recovers its original temperature—at first carbon is deposited, but as soon as the blast is sent in, the deposit is burnt off by the non-luminous flame, and the tube becomes fully red—the whole operation not occupying more than ten minutes or a quarter of an hour.

## VI.—*Note on the Quantitative Determination of Sulphur.*

### By Dr. David S. Price, F.C.S.

My object in communicating the following brief note to the Society is to direct attention to a source of error which has hitherto escaped notice in the estimation of sulphur, where fusion of the substance with nitre is the process employed.

The method by fusion is generally conducted in a gold crucible or platinum dish over the gas-flame. Now, I have found that unless great care be taken to prevent the fused mass passing over to the outside of the vessel, and so coming in contact with the flame or products of combustion, an appreciable and, in some cases, serious error will arise, owing to the sulphuric acid produced from the sulphurous acid in the flame—a product of the oxidation of the bisulphide of carbon contained in the gas—combining with the potassa of the fused salt.

I have made several experiments to ascertain the amount of error that may be occasioned from the above cause, but it will not be necessary for me to describe more than one:—

In this instance, the flame issuing from a Bunsen's burner was made to strike against a little fused nitre on the under-side of a small platinum dish, when, in three-quarters of an hour, as much sulphuric acid was obtained as is equivalent to 12 milligrammes of sulphur—a quantity larger than is contained in 5 grammes of grey pig-iron.

In fusing pig-iron with nitre, a process recommended by some for the estimation of the sulphur it contains, the mass, especially if the iron be rich in manganese, invariably creeps over to the outer walls of the crucible, and it is therefore impossible to obtain correct results when the operation is conducted over the gas flame.

As a check on the experiments, nitre was fused by the flame of the spirit-lamp, when, as was to be anticipated, not a trace of sulphuric acid could be detected upon the addition of a barium-salt to the aqueous solution of this fused mass, rendered acid by hydrochloric acid.

## VII.—*On the Combustion of Iron in Compressed Oxygen.*

By E. Frankland, F.R.S.

Whilst oxygen was being compressed into a Natterer's apparatus, recently supplied to the Royal Institution from Vienna, an accident occurred, which deserves to be placed on record, owing to the interesting relations of iron to highly compressed oxygen revealed by it. The accident occurred in the following manner:—Oxygen was liberated from pure chlorate of potash, heated in a florence flask, and was collected in a floating bell-gasholder, whence it was drawn through a flexible tube, and pumped in a strong wrought-iron receiver, of ·62 litre capacity, and weighing 2·775 killogrammes. When about 25 atmospheres of oxygen had thus been introduced into the receiver, a sharp explosion occurred, followed by a shower of brilliant sparks, which lasted for several seconds. On examining the apparatus, it was found that the union-joint connecting the pump with the receiver, had given way, allowing the compressed gas to escape from the latter. The pump-head, containing the valve, was slightly scorched internally. The steel tube connecting this head with the receiver, was very hot, and had obviously been in a state of active combustion, as it was coated internally with a layer of fused oxide of iron, whilst its bore had increased to at least three times its original size, and in two places the tube was even perforated. The receiver was also heated, although not to such an extent as to be unbearable to the hand. On examining its interior, it was found that the combustion had been propagated to the steel cap, the narrow passage in which was hollowed out into a capacious chamber, whilst the steel screw-valve had been completely consumed. The combustion had not, however, stopped here, but, extending into the receiver itself, had seized upon the internal walls of the latter, and covered them with fused globules of magnetic oxide of iron, and there can scarcely be a doubt, that, had the union-joint not given way, and thus furnished an outlet for the compressed oxygen, the latter would, in a few seconds more, have converted the receiver into a most formidable shell, the almost inevitable explosion of which would have scattered fragments of intensely ignited iron in all directions.

Regarding the primary cause of this explosion, there can scarcely be two opinions. The piston and valves were lubricated with olive oil, and the latter, becoming ignited by the heat of the compressed gas, had communicated its combustion to the steel and iron of the apparatus. Although the pump and receiver were not artificially cooled, yet this circumstance did not in all probability contribute materially to the ignition, because the oxygen was very slowly pumped into the receiver, the operation having to be frequently interrupted, to wait for the necessary quantity of gas which was being contemporaneously generated. Moreover, I had ascertained, immediately before the explosion, that the receiver was quite cold, and the head of the pump only just perceptibly warm. A few days previously, 60 atmospheres of oxygen had been with impunity *rapidly* pumped into the same receiver, and equally without any external refrigeration. How, then, is this difference of result to be accounted for? The answer to this question is not difficult, when an apparently trivial alteration of the condition of the apparatus, in the two operations, is known. In the directions for the use of Natterer's apparatus, contained in the article "Kohlensäure" (*Handwörterbuch der Chemie*, Band. iv,) the writer states, that before the pumping commences, the space between the piston and the valve should be filled up with oil, so as to prevent the retention of any gas between the piston and valve, when the former, in compressing, is pushed to the extreme limit of its stroke. Any gas so remaining in such space (*schädlicher Raum.*), expands again on the return of the piston, and thus causes, if not an actual loss of power, at least a considerable retardation in the compressing process. In the operation above described, in which 60 atmospheres were compressed with impunity into the receiver, I omitted to follow this part of the directions of the *Handwörterbuch*, whilst in the subsequent experiment in which ignition occurred, a layer of olive oil, about 0·1 inch thick, was poured upon the piston, so as exactly to fill the space above mentioned.

Now, a careful examination of the burnt parts of the apparatus, leaves no doubt that the combustion commenced in the space between the piston and valve, and that it was this layer of oil which first became ignited. The compression of oxygen to $\frac{1}{75}$th of its volume should, according to thermo-mechanical laws, raise the temperature of the oxygen to upwards of 2,000° C., but after making due allowance for the loss of heat to surrounding surfaces, there still remains a temperature sufficiently high for the ignition of oil under favourable circumstances. If the oil be spread as a thin film upon the surface of a mass of metal, the rapid absorption heat by the latter prevents the temperature of the oil from ris to its igniting point; but, in the form of a layer, 0·1 inc thickness, no such rapid refrigeration can occur, and the face of the oil, in contact with the gas, may become ignited by the rapid communication to it of the high temperature of the compressed oxygen. It is also not improbable, that traces of chlorate of potash, which are always carried over with oxygen when the latter is rapidly evolved, may have found their way into the pump, and contributed, to some extent, to the ready inflammability of the oil. However this may be, the result ought to be regarded as a caution against the use of combustible lubricants in the compression of oxygen or nitrous oxide. If ignition of the oil occur at high pressures, it will assuredly be communicated to the iron of the receiver, which evidently burns in oxygen compressed 25 times, with at least the same facility as tissue-paper in atmospheric air, the condition of the various parts of the apparatus, after the explosion, leading to the conclusion, that the combustion from the beginning to end, occupied only a very short time, probably not more than 3 or 4 seconds. The risk attending the compression of oxygen and nitrous oxide, may be avoided by the employment of a non-combustible lubricant. For this purpose, a strong solution of soft-soap in distilled water, appears to answer very well.

The facility with which a mass of iron thus becomes ignited, and the rapidity with which it burns in oxygen, at high pressures, suggests the possibility of employing shells of wrought or cast-iron charged with compressed oxygen, for warlike purposes. The interior of such a shell would scarcely be more difficult to ignite than gunpowder, and, once ignited, the pressure of the enclosed oxygen would, notwithstanding its absorption, be for some time augmented by the intense heat, whilst the walls of the shell would become thinner, until they finally burst into fragments of burning and semi-molten iron. The condition necessary to secure such a result, may be determined from the known absolute thermal effect of iron in oxygen. Andrews found that the union of one litre of oxygen with iron, produces sufficient heat to raise the temperature of 5,940 grammes of water through 1° C. It hence follows, that 780 cubic inches of oxygen, by combination with iron, would evolve sufficient heat to raise 1 lb. of cast-iron to its melting point. This amount of oxygen introduced into the receiver above described, would exert a pressure of 20·5 atmospheres, consequently it would require the union of a quantity of oxygen exerting a pressure of 125 atmospheres, to raise the whole of the receiver to the melting point of cast-iron. These conditions are not encouraging; for, although a less amount of oxygen than that required for the complete fusion of the shell would suffice for the purpose required, yet, it would doubtless be necessary to augment the thickness of such a vessel when used as a projectile, and this would necessitate a corresponding increase in the bursting charge of oxygen. Thus, little could probably be effected with less than 100 atmospheres of oxygen forced into the shell,—a pressure, which, I fear, would prove not only dangerous, but unmanageable.

## VIII.—*Researches on the Physiological Variations of the Quantity of Hippuric Acid in Human Urine.*

By J. L. W. THUDICHUM, M.D.

THE following researches were made upon the urine of a healthy man weighing 10 stone, 7lbs., and eating a moderate amount of good mixed diet. He led an active life, and during the inquiry was, on an average, at work during sixteen hours out of the twenty-four.

1. On August 17th, at 9 o'clock a.m., there had been collected 1370 c.c. of urine from the previous twenty-four hours. Sp. gr. 1017. 200 c.c. treated with hydrochloric acid yielded uric acid 4·1 grains. The whole quantity of urine contained 28·7 grammes of urea, estimated by nitrate of mercury. 500 c.c. were evaporated on the water-bath, treated with hydrochloric acid, ether, and a little alcohol; the extraction was repeated with six portions of ether; the united ethereal extracts were washed with small portions of water, and then reduced by distilling off the ether; the residue was precipitated by a little water, allowed to stand for crystallisation, the crystals were collected on a filter, washed with cold water, dried in the water-stove, and weighed in covered glasses. There were obtained 0·516 grammes of hippuric acid, corresponding to 1·413 grammes, or 21·9 grains, as the total amount of acid contained in the whole twenty-four hours' urine. The water with

which the ether had been washed was evaporated and set aside for crystallisation; it yielded 0·126 grammes, or 1·958 grains, of hippuric acid. This addition swells the calculated amount of hippuric acid in the day's excretion to 1·758 grammes.

This analysis demonstrated clearly that the analytical proceeding had to be changed, so as to avoid the loss occasioned by washing with water the ethereal solution containing alcohol. This was effected by evaporating the extract of the urine to a stiff syrup, working it into a stoppered bottle while warm, taking up the last residues with the necessary amount of hydrochloric acid, and shaking briskly with large quantities of dry ether. In this manner the extract and ether separated almost immediately, and required but rarely the addition of alcohol. The ether took up much less urea than it would have done had it contained alcohol. After distillation, a small quantity of reddish-yellow residue was obtained, which was mixed with a little water and allowed to crystallise. The crystals were always washed until the washings were colourless, next dried by pressing between blotting-paper, exposure to air, then by keeping over sulphuric acid, and ultimately by drying at 100° C. in the water-oven. This proceeding was carried out in all subsequent examinations.

2. August 18th. 1580 c.c. contained 30 grm. of urea; 200 c.c. yielded 3·1 grains of uric acid; 500 c.c. yielded 0·282 grm. of hippuric acid, corresponding to 0·891 grm. or 13·81 grains per day.

3. August 19th. 1720 c.c. contained 30·96 grm. of urea; 500 c.c. yielded 1·3 grains of uric acid; 500 c.c. yielded 0·203 grm. of hippuric acid, equal to 0·698 grm., or 10·819 grains, per day.

4. August 20th. 1600 c.c. urea = 28·8 grm.; uric acid; 1·6 grains; hippuric acid in 500 c.c. = 0·178 grm., equal to 0·569 grm., or 6·82 grains, per day.

5. August 21st. 1525 c.c., the whole evaporated for hippuric acid.

$$\left.\begin{array}{l}\text{The 1st 6 ozs. of ether extracted } 0{\cdot}433\\ \text{The 2nd 6 ozs. of ether extracted } 0{\cdot}110\\ \text{The 3rd 6 ozs. of ether extracted } 0{\cdot}060\end{array}\right\}\ 0{\cdot}603 \text{ grm. or } 9{\cdot}35 \text{ grains.}$$

There was a firm sediment in the bottle, so that a little hippuric acid may have escaped extraction.

6. August 22nd. 1345 c.c. and estimated loss of 155 c.c., total 1500 c.c. The entire amount evaporated for analysis.

The 1st 6 ozs. of ether extracted 0·19 grm.

The 2nd 6 ozs. of ether extracted 0·127 grm. {very pure and shining crystals

The 3rd extraction with ether and alcohol yielded no hippuric acid.

| | | |
|---|---|---|
| Total obtained............ | 0·317 grm. | = 4·9 grains. |
| Add 10 per cent. for loss.... | 0·0317 grm. | |
| Total in 24 hours ........ | 0·3489 grm. | = 5·4 grains. |

This decrease of the quantity of hippuric acid from the large amount discovered on August 17th in obs. 1, exciting attention, it was remembered that the experimenter had, on August 16th, eaten some greengage tart at dinner. In order to test whether the large amount in obs. 1 was really due to this cause, he ate twelve hard, scarcely ripe greengages in the evening of the 22nd.

7. August 23rd. 1470 c.c. The whole evaporated yielded:

| | |
|---|---|
| On 1st extraction.... | 0·437 grm. |
| On 2nd extraction.... | 0·438 grm. |
| On 3rd extraction.... | 0·162 grm. |
| Total........ | 1·037 grm. or 15·5 grains. |

On a fourth extraction by 6 ounces of ether, a trace of hippuric acid was still obtained. This, together with the result of the fourth extraction of the residue of No. 6, weighed 0·015 grm. He ate six greengages with tart at dinner, having eaten five after breakfast. In the evening he ate again six French ones—fine, ripe, slightly bitter.

8. August 24th. 2150 c.c.; loss of 150 c.c. thrown away to ease the bladder while out. The entire amount evaporated gave:

| | |
|---|---|
| 1st extraction................. | 1·537 grm. |
| 2nd extraction .............. | 0·234 grm. |
| 3rd extraction................ | 0·169 grm. |
| Total................ | 1·940 grm. |

To this must be added the amount of acid lost in the 150 c.c. of urine, which will bring it to upwards of 2 grammes.

9. August 25th. 1420 c.c. hippuric acid = 0·450 grm. The second extraction yielded nothing.

10. August 26th. 1670 c.c.

| | | |
|---|---|---|
| 1st extraction .......... | 0·380 grm. | |
| 2nd extraction .......... | 0·242 grm. | very pure |
| 3rd extraction .......... | 0·096 grm. | very pure |
| Total ............ | 0·718 grm. | |

11. August 27th. 2200 c.c.

| | |
|---|---|
| 1st extraction ................ | 0·360 grm. |
| 2nd extraction .............. | 0·056 grm. |
| Total ............. | 0·416 grm. |

On the evening of this day the experimenter again ate some greengages.

12. August 28th. 1600 c.c.; hippuric acid, 0·627 grm. It was very dark, and on drying in the water-oven, yielded a sublimate of benzöic acid. The laboratory was filled with the smell of this acid. The experimenter ate again some greengages on this day.

13. August 29th. 2200 c.c.; hippuric acid, first extract 1·063 grm. There was a little benzoic acid sublimed upon the cover. The second and third extraction yielded nothing.

14. August 30th. 1050 c.c.; of this 800 c.c. evaporated, yielded 0·129 grm. of hippuric acid in fine crystals. Total for 1050 c.c. = 0·169 grm. Second extraction yielded nothing.

15. August 31st. 1450 c.c. hippuric acid 1·144 grm. On this day the inquirer ate a pint of greengages.

16. September 1st. The urine from twenty-four hours amounted to 1260 c.c. It yielded a very dark extract, from which 1·405 grm. of hippuric acid were obtained.

17. September 2nd. 1860 c.c.; hippuric acid = 1·129 grm. A pint of fine ripe greengages were eaten on this day.

18. September 3rd. 1850 c.c.; hippuric acid 2·212 grm.

19. September 4th. 1600 c.c.; hippuric acid 0·507 grm.

20. September 5th. 1780 c.c.; hippuric acid 0·315 grm.

These results clearly show that, while the ordinary amount of hippuric acid excreted by the person under observation may vary between from 0·169 to 0·315 and 1·0 grm., this quantity will be regularly increased after eating greengages, and in proportion to the number or quantity of greengages consumed.

During the evaporation of the urine voided after the eating of greengages, it was observed that some benzoic acid was volatilised, and crystallised on the surface of the paper with which the dish was covered. I am of opinion that this benzoic acid was present in the urine as such.

The above experimental data constitute an episode in a longer essay on the physiology of hippuric acid, which will be published elsewhere.

---

## IX.—*On the Photographic Transparency of various Bodies, and on the Photographic Effects of Metallic and other Spectra obtained by means of the Electric Spark.*

By W. A. MILLER, M.D., LL.D., Treas. and V.P.R.S., Professor of Chemistry in King's College, London.

[From the Philosophical Transactions, 1863, 1].

1.—At a Meeting of the British Association held in Manchester in the autumn of 1861, I exhibited some photographs of spectra from the spark obtained between wires of different metals by means of an induction-coil. Upon this occasion a hollow prism filled with bisulphide of carbon was employed, because, owing to its great dispersive power, it furnished spectra in which the lines under examination were more widely separated, and exhibited with greater distinctness than by any other medium in ordinary use.

Plate xxxix, Fig. 30 exhibits a copy of the photograph of the solar spectrum obtained by means of a hollow glass prism filled with bisulphide of carbon, contrasted with the spectrum obtained through the same prism simultaneously, from the spark between copper terminals of the secondary coil in the induction apparatus. In this, and in all the subsequent figures, the less refrangible end of the spectrum is upon the left-hand side of the Plate.

The great prolongation of the more refrangible portion of the spectrum beyond the part visible to the unaided eye, led me to believe that the bisulphide was a material which exerted but little absorbent action upon the chemical rays. Subsequent experiments have, however, convinced me that this opinion was erroneous, and have rendered it necessary to modify considerably the conclusions deduced from those experiments.

2. At the time that that paper was written, I believed that the photographic effects produced by the electric spectra of all the metals furnished results in a great degree similar to each other, if

not actually identical. This, it will be seen from subsequent statements, is correct so far as the fact of the similarity in this portion of the spectra is concerned, but is erroneous as regards the general conclusion deduced from it. During the past winter, I have renewed these experiments, substituting a quartz-train for glass and bisulphide of carbon, and have chiefly used a fine quartz prism, kindly lent to me by my friend Mr. Gassiot. The refracting angle of this prism is about 60°; its faces are about 2 inches long and $1\frac{5}{8}$ inch broad, and are so cut as to furnish a singly refracted beam for the medium rays, by transmitting it along the axis of the crystal. It is well-known, from the experiments of Prof. Stokes* and M. E. Becquerel, that quartz is remarkable for its transparency to both fluorescent and phosphorogenic rays of high refrangibility. It was soon evident that the absorbent action of the bisulphide was far greater than I had imagined, and that in reality the spectrum which it transmitted was composed of rays which did not extend beyond one-tenth or one-twelfth of the entire length of the spectrum obtained by the use of a quartz-train.†

3. The dispersive power of rock-crystal is, however, comparatively low, and the difficulty of obtaining with it a spectrum free from the effects of double refraction through its entire length is great; so that it appeared to be worth while, as a preliminary inquiry, to ascertain whether any singly refracting medium could be procured, better adapted to researches of this nature by sufficient permeability to the chemical rays, and by tolerably high dispersive power. Although no material on the whole preferable to quartz has been found, the investigation gave results of considerable interest.

4. Before proceeding to detail these results, it will, however, be convenient, as several distinct subjects will be discussed in this

---

* Phil. Trans. 1852, p. 540.

† The absorptive power of the bisulphide for the chemical rays was, however, noticed by M. E. Becquerel as far back as 1843, as I find by again referring to his paper (*Annales de Chimie*, sér. 3, vol. ix, p. 301). In this paper, M. Becquerel describes the absorbent action of various solids and liquids upon the chemical rays, but, from having used solar light, he failed to remark the great difference between the absorptive powers of quartz and glass. Although he used prisms of rock-salt, rock-crystal, and alum, his results do not indicate the real difference in their absorptive power: and, as in all his experiments on liquids, he employed a vessel with flint-glass sides to hold them, his conclusions are vitiated by the same error which affected my own earlier inquiries on the subject.

paper, to state the order in which I propose to arrange my remarks, and the heads to which they will be referred.

I shall commence with

(1) *The absorption of chemical rays by transmission through different media.*

*a.* By transmission through solids.

*b.* By transmission through liquids.

*c.* By transmission through gases and vapours.

(2) *The absorption of the chemical rays by reflection* from polished surfaces.

(3) *The photographic effects of the electric spectra of different metals taken in air*, including.

*a.* Pure metals.

*b.* Alloys.

(4.) *Photographic effects of electric spectra of different metals produced by transmitting the sparks through gases other than atmospheric air.*

5. The general results of my experiments upon the absorption of the chemical rays are the following: —

(1) Colourless bodies which possess equal powers of transmitting the luminous rays vary greatly in permeability to the chemical rays.

(2) *Diactinic* solids (that is to say, solids which are permeable to the chemical rays) preserve their diactinic power both when liquefied and when converted into vapour.

(3) Colourless solids which are transparent to light, but which exert a considerable absorptive effect upon the chemical rays, preserve their absorptive power with greater or less intensity both in the liquid and the gaseous state (21).

Whether the compound be dissolved in water or be liquefied by heat, these conclusions are equally true as regards liquids. Water is perfectly permeable to the chemical rays; and this circumstance, conjoined with the fact that in no instance does the process of solution seem to interfere with the special action of the substance dissolved upon the incident rays, renders it practicable to submit to trial a great number of bodies which it would otherwise be impossible to subject to experiments of this nature, owing to the extreme difficulty of obtaining them in crystals of sufficient size and limpidity.

## § 1. ABSORPTION OF THE CHEMICAL RAYS.

### a. *By Transmission through Solids.*

6. The general arrangement of the apparatus employed in this inquiry is represented in Fig. 1, in which the observer is supposed to be looking down upon the instrument: *c c* is a camera which allows of a considerable range of adjustment, and is attached to a cylindrical box, within which is a prism *b*, of rock crystal. At *l* is a quartz lens of 1¼-inch aperture, and 17¼ inches focal length. At one end of the tube *t*, which can be lengthened or shortened by a sliding joint, is a slit *s*, provided with a screw for regulating the width of the opening. This slit is arranged parallel to the axis of the prism, and in these experiments was adjusted to a distance of 37 inches from the lens *l*. The prism is placed at about its angle of minimum deviation for the mean ray, and, for facility of

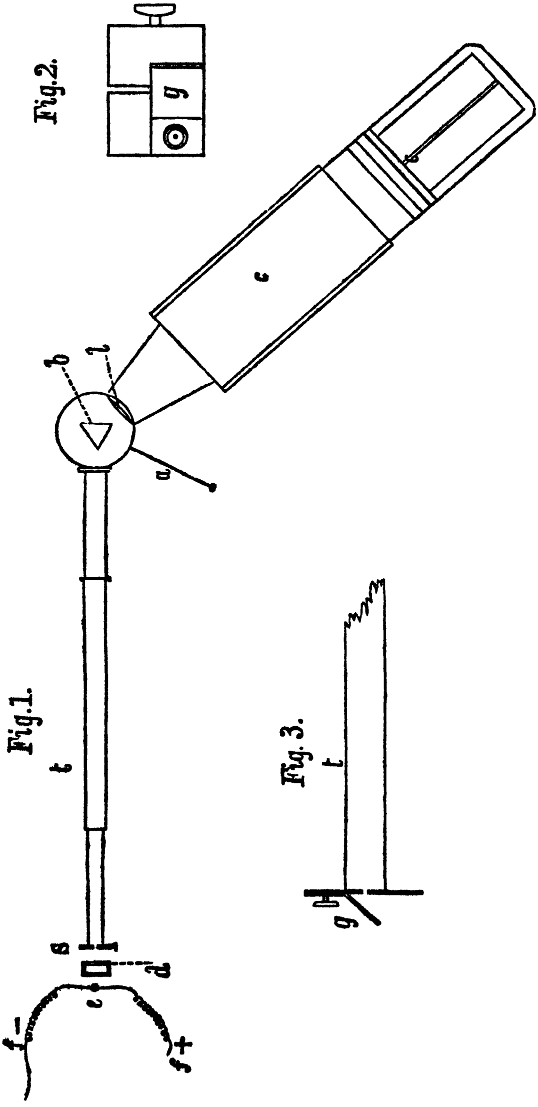


Fig. 2.
Fig. 1.
Fig. 3.

manipulation, can be turned round upon its own axis by means of the lever *a*. The angle formed between the camera and the tube *t* also admits of variation, as circumstances may require. At *d* is placed the substance the transparency of which is to be tested; and at *e* are the metallic electrodes, which are connected with secondary wires *f f* of a 10-inch induction coil, not shown in the figure. The wires of the coil terminate in electrodes composed of fine silver. The coil was excited by means of a battery consisting of five elements of Grove's construction, a condenser being included in the primary circuit, whilst a small Leyden jar, exposing about 75 square inches of metallic coating upon each of its surfaces, was introduced into the secondary circuit. In this way a torrent of sparks could be maintained between the electrodes at *e*, without any sensible variation of power, for ten minutes at a time, or longer if necessary. In these experiments, an exposure of the sensitive plate for five minutes in the camera was requisite.

At a suitable distance behind the lens (about 26 inches*), a collodion plate coated with iodide, or occasionally with a mixture of iodide and bromide of silver, was supported in the camera, for the purpose of receiving the image of the spectrum†. The plate was excited by the use of a bath of nitrate of silver containing 30 grains of the nitrate to an ounce of water. The image was developed in the usual way by means of pyrogallic acid, in the proportion of one grain to the ounce of water, and fixed with cyanide of potassium.

7. The spectra of electric sparks so obtained were remarkable for their great length; indeed they extended beyond the termina-

---

* This distance was found by experiment to give nearly a flat field, with the image of the slit formed by all the different rays in focus simultaneously. My friend and colleague, Professor J. C. Maxwell, kindly calculated for me the relative positions of lens and prism necessary to ensure an approximatively flat field for the visible rays.

If the lens be placed between the slit and the prism, a very great difference occurs between the points of convergence of the most refrangible and the least refrangible rays, amounting with the lens and prism which I used to nearly 14 inches. When the lens is before the prism, both coincide in augmenting the convergence of the more refrangible rays; whereas when the lens is placed behind the prism, as shown in the figure, the convergence occasioned by the lens is neutralized by the prism, which now acts in the opposite direction upon the diverging rays as they fall upon it from the slit.

† My friend Mr. Pizey, who assisted me in those experiments, prepared the collodion for me, following nearly the directions given by Hardwich in his 'Manual of Photographic Chemistry,' 6th edition, p. 262. It was iodized with a mixture of equal parts of iodides of potassium and cadmium, and was perfectly uniform in its action, even for weeks after it had been iodized, if kept in the dark.

tion of the visible rays for a space equal to five or six times the length of the luminous portion.

For the convenience of comparing the results of the various experiments together, I have adopted an arbitrary fixed scale, the fiducial point of which is the line H in the solar spectrum. Calling this 100, the more refrangible rays are numbered onwards, and the less refrangible rays backwards from it, the line B in the solar spectrum being at 84; the length of the spectrum from silver points extends from 96·5 upon this scale to 170·5. The solar spectrum for the purpose of this comparison was projected upon the collodion plate by means of a small mirror of polished steel (*g*, Fig. 3) placed so as to form an angle of 45° with the surface of the plate carrying the slit, and to cover a portion of the vertical slit, as shown by an end view of the tube at *g*, Fig. 2, whilst the direct image from the silver points fell simultaneously, parallel to that of the solar spectrum, upon the collodion plate in the camera.

8. The following Table contains a list of the various substances subjected to experiment. All these bodies allowed the less refrangible rays to pass, but cut off the rays of medium and extreme refrangibility wherever absorption occurred at all.

TABLE I.—*Diactinic Power of Solids.*

| Name of substance. | Thickness, in inches. | Termination of spectrum. | Relative lengths of spectra. | Remarks. |
|---|---|---|---|---|
| Ice .................... | about 0·5 | 170·5 | 74·0 | |
| Diamond* (*l*) ............ | 0·032 | 155 5 | 59 0 | |
| Diamond (*m*) ............ | 0·017 | 159 5 | 62·0 | |
| Diamond (A) ............ | 0·182 | 115·5 | 19·0 | |

---

* I am indebted to my friend Professor W. H. Miller, of Cambridge, for the opportunity of examining the diamonds and sapphires alluded to above. *l* was a slice of diamond bounded by cleavage-planes, from the Warburton Collection. *m* a somewhat thinner slice from the same collection. A a large octahedral diamond from the Humian Collection: all these were colourless. The sapphire 24 was a large six-sided prism from the Brooke Collection; that marked B was a smaller prism of a faint bluish tinge from Professor Miller's own collection. *n* is a colourless crystal of sapphire from the Warburton Collection. I made an application to the Trustees of the British Museum for permission to use some of the limpid specimens in their collection, but was informed that, even for such a purpose, the Act of Parliament forbids them to allow any mineral to pass off their premises. Mr. Maskelyne was kind enough to lend me a fine colourless topaz from his own collection.—[Feb., 1863.]

## TABLE I (*continued*).

| Name of substance. | Thickness, in inches. | Termination of spectrum. | Relative lengths of spectra. | Remarks. |
|---|---|---|---|---|
| pphire (24)............ | 0·13 | 116·0 | 19·5 | |
| pphire (B) ............ | 0·093 | 112·0 | 15·5 | Faint bluish tinge. |
| pphire (*n*) ............ | 0·12 | 111·0 | 14 5 | |
| artz ................ | 0·16 | 170·5 | 74·0 | With quartz-train. |
| White Topaz ............ | 0·19 | 162·0 | 65·5 | Faint image of spectrum. |
| Mica ................. | 0·007 | 114·5 | 18·0 | |
| Oil of vitriol ............ | 0·75 | 160·5 | 64·0 | |
| ulphate of lime (solid) .. | about 0·3 | 155·5 | 59·0 | |
| ulphate of baryta (solid).. | about 0·4 | 154·5 | 58·0 | |
| ulphate of magnesia (solid). | 0·34 | 158·0 | 61·5 | |
| ulphate of potash........ | Sat. soln. 0·75 in. | 159·5 | 63·0 | |
| ulphate of soda ........ | " | 159·5 | 63·0 | |
| ulphate of ammonia .... | " | 145·5? | 49·0? | |
| ulphate of zinc.......... | " | 152·5 | 56 0 | |
| Alum .................. | " | 159·5 | 63·0 | |
| ulphate of iron.......... | " | 105·0 | 8·5 | Pale green. |
| ulphate of manganese.... | " | 144·5 | 48·0 | Faint pink. |
| ulphate of copper ...... | " | 112·5 | 16·0 | Full blue. |
| ulphite of soda.......... | " | 127·5 | 31·0 | |
| Hyposulphite of soda .... | " | 108·5 | 12·0 | |
| Fluor-spar .............. | 0·17 | 170·5 | 74·0 | |
| Fluoride of sodium ...... | Sat. soln. 0·75 in. | 159·5 | 63·0 | |
| Fluoride of ammonium.... | " | 166·5 | 70·0 | |
| Hydrochloric acid, sp. gr. 1·1 | 0·75 in. | 152·5 | 56·0 | |
| Rock-salt (solid).......... | 0·75 | 159·5 | 63 0 | |
| Chloride of potassium .... | Sat. soln. 0·75 in. | 159·5 | 63·0 | |
| Chloride of ammonium.... | " | 155·0 | 58·5 | |
| Chloride of barium ...... | " | 153·0 | 56·5 | |
| Chloride of strontium .... | " | 152·0 | 55·5 | |
| Chloride of calcium ...... | " | 147·0 | 50·5 | |
| Chloride of zinc.......... | " | 145·5 | 49·0 | |
| Chloride of manganese.... | " | 104·5 | 8·0 | Faint rose colour. |
| Chloride of tin (SnCl) .... | " | 108·5 | 12 0 | Spectrum cut off abruptly. |
| Chloride of tin (SnCl ) .... | Strong solution. | 114·5 | 18 0 | Spectrum cut off abruptly. |
| Chloride of arsenic ($AsCl_3$) | Liquid. | 101·5 | 5·0 | Spectrum cut off abruptly. |
| Corrosive sublimate ...... | Sat. soln. 0·75 in. | 128·5 | 32·0 | Spectrum cut off abruptly. |
| Bromide of sodium ...... | " | 144·5 | 48·0 | |
| Bromide of potassium .... | " | 144·5 | 48·0 | |
| odide of sodium ........ | " | 114·5 | 18·0 | Spectra terminate abruptly. |
| odide of potassium ...... | " | 114·5 | 18·0 | |
| yanide of potassium .... | " | 105·5? | 9·0? | Prepared by Liebig's process. |
| yanide of mercury ...... | " | 145·5 | 49·0 | |

TABLE I (*continued*).

| Name of substance. | Thickness, in inches. | Termination of spectrum. | Relative lengths of spectra. | Remarks. |
|---|---|---|---|---|
| Sulphocyanide of potassium | Sat. Soln. 0 ·75 in. | 112 ·5? | 16 ·0? | Slightly yellowish. |
| Hydrate of soda.......... | „ | 131 ·5 | 35 ·0 | From sulphate by p<br>pitation with baryt |
| Hydrate of potash........ | „ | 129 ·5 | 33 ·0 | |
| Hydrate of ammonia...... | Sp. gr. 0 ·945 | 170 ·5 | 74 ·0 | Rather feeble spectru |
| Hydrate of baryta........ | Sat. soln. 0 ·75 in. | 158 ·0 | 61 ·5 | |
| Hydrate of strontia ...... | „ | 150 ·0 | 53 ·5 | |
| Hydrate of alumina ...... | Strength of solution not determined. | 146 ·0 | 49 ·5 | Crum's solution. |
| Hydrate of silica ........ | | 152 ·0 | 55 ·5 | Dialysed from hy<br>chloric solution. |
| Carbonate of soda ........ | Sat. soln. 0 ·75 in. | 146 ·0 | 49 ·5 | |
| Carbonate of potash ...... | „ | 146 ·0 | 49 ·5 | From ignited bicarbo |
| Iceland spar ............ | 0 ·35 | 160 ·0 | 63 ·5 | |
| Bicarbonate of soda ...... | Sat. soln. 0 ·75 in. | 145 ·0 | 48 ·5 | |
| Bicarbonate of potash .... | „ | 142 ·0 | 45 ·5 | |
| Sesquicarbonate of ammonia | „ | 152 ·0 | 55 ·5 | |
| Boracic acid ........... | „ | 143 ·0 | 46 ·5 | Faint beyond 109. |
| Borax ................. | „ | 158 ·5 | 62 ·0 | |
| Phosphoric acid .......... | „ | 117 ·5? | 21 ·0 | |
| Phosphate of soda ($HO,2NaO,PO_5$)...... | Solution of 60 grains of dried salt in 1 oz. of water. | 156 ·5 | 60 ·0 | Equal weights of sa<br>salt: one dried at 3<br>F., the other ignite |
| Pyrophosphate of soda $2NaO,PO_5$ .......... | | 156 ·5 | 60 ·0 | |
| Triarseniate of soda ($3NaO,AsO_5$) ........ | Sat. soln. 0 ·75 in. | 127 ·5 | 31 ·0 | |
| Arsenic acid ........... | „ | 119 ·5 | 23 ·0 | |
| Chlorate of potash........ | „ | 145 ·5 | 49 ·0 | |
| Nitric acid .............. | Sp. gr. 1 ·3 | 106 ·5 | 10 ·0 | Colourless. |
| Nitrate of soda .......... | Sat. soln. 0 ·75 in. | 112 ·5 | 16 ·0 | All the spectra of the<br>trates are cut off sharp |
| Nitrate of potash ........ | „ | 112 ·5 | 16 ·0 | |
| Nitrate of ammonia ...... | „ | 112 ·5 | 16 ·0 | |
| Nitrate of lime .......... | „ | 112 ·5 | 16 ·0 | |
| Nitrate of magnesia ...... | „ | 112 ·5 | 16 ·0 | |
| Nitrate of baryta ........ | „ | 111 ·5 | 15 ·0 | |
| Nitrate of strontia ...... | „ | 111 ·5 | 15 ·0 | |
| Nitrate of nickel ........ | „ | absorbed | 0 ·0 | Intense green solution |
| Nitrate of lead .......... | „ | 111 ·5 | 15 ·0 | |
| Subnitrate of mercury .... | „ | 111 ·5 | 15 ·0 | |
| Nitrate of silver ........ | „ | 106 ·0 | 9 ·5 | |
| Acetic acid .............. | Glacial, liquefied. | 112 ·5 | 16 ·0 | Spectrum ends abrupt |
| Acetate of soda.......... | Sat. soln. 0 ·75 in. | 144 ·5 | 48 ·0 | |
| Acetate of potash ........ | „ | 113 ·5? | 17 ·0? | |
| Acetate of ammonia ...... | „ | 144 ·5 | 48 ·0 | |
| Acetate of baryta........ | „ | 115 ·5? | 19 ·0? | Very faint brown<br>tinge in liquid. |
| Acetate of lime .......... | „ | 115 ·5? | 19 ·0? | |
| Acetate of lead .......... | „ | 130 ·5 | 34 ·0 | |

TABLE I (*continued*).

| Name of substance. | Thickness, in inches. | Termination of spectrum. | Relative lengths of spectra. | Remarks. |
|---|---|---|---|---|
| artaric acid ............ | Sat. Soln. 0·75 in. | 127·5 | 31·0 | |
| rtrate of soda.......... | „ | 144·5 | 48·0 | |
| Tartrate of potash........ | „ | 144 5 | 48·0 | |
| Rochelle salt (NaO,KO, $C_8H_4O_{10}$)............ | „ | 144 5 | 48·0 | |
| Tartar emetic (KO,$SbO_3$ $C_8H_4O_{10}$)............ | „ | 181·5 | 35·0 | |
| Citric acid .............. | „ | 183·5 | 37·0 | |
| Oxalic acid.............. | „ | 114·5 | 18·0 | |
| Oxalate of potash ........ | „ | 117·5 | 21·0 | |
| Oxalate of ammonia...... | „ | 124·5 | 27·0 | |
| Sugar candy .......... | 60 grains in 200 grains of water. | 156·5 | 60·0 | |
| Milk-sugar............ | | 151·5 | 55·0 | |
| Gum arabic.............. | Mucilage. | 113·5? | 16·0 | Slightly opalescent. |
| Silicate of soda .......... | Sat. soln. 0·75 in. | 108·5 | 12·0 | |
| Faraday's optical glass .... | 0·54 | 101·5 | 5·0 | Pale yellow. |
| Flint glass .............. | 0·68 | 105·5 | 9·0 | |
| Window sheet glass ...... | 0·07 | 112 5 | 16·0 | |
| Hard Bohemian glass .... | 0·18 | 114 5 | 18·0 | |
| Plate glass ...... ....... | 0·22 | 111·5 | 15·0 | |
| Crown glass ............ | 0 74 | 106·5 | 10·0 | Greenish. |
| Thin glass for microscope.. | 0·009 | 116·5 | 20·0 | |

The photographic impression of each spectrum, in every case quoted in this Table, commences at 96·5, and the number inserted in the Table in the second column of figures, indicates the point at which the most refrangible rays transmitted by the compound under examination ceased. The numbers in the third column of figures represent the length of the spectrum, the unit of the scale being one millimetre.

9. In the majority of cases of saline compounds in the foregoing Table, the results given are those obtained by forming a saturated solution of the compound in distilled water, and decanting the liquid after it had become clear by standing. It is not advisable to filter in these cases, as the introduction of minute quantities of certain compounds, especially of some of organic origin, greatly impairs the transparency of the liquid to the rays which produce chemical action.

The solution, duly prepared, was then placed in a small trough made by cutting a notch in a piece of plate-glass ¾ inch in thickness, the sides of the trough being completed by thin plates of polished quartz, which were pressed by means of bands of caoutchouc against the ground surfaces of the plate-glass. No cement was employed, and the trough was taken to pieces and cleansed between each experiment, a stratum of liquid 0·75 inch thick being used in each case.

10. In the preparation of the various compounds for examination, much care was taken to employ the materials in a state of purity. In one or two instances, however, it has happened that an acid which usually forms highly diactinic salts has exhibited an anomalous and excessive absorptive power, although in combination with a base which in other instances furnishes strongly diactinic salts. Here some impurity, in quantity so small as to escape the tests in ordinary use, but sensitive to the action of light, has probably been present, and has impaired the diactinic capacity of the substance. Cases in which such impurity is suspected, are indicated in the Table by the mark (?) subjoined to them.

It may here be observed, that the solution of a salt in water always to a certain extent impairs the diactinic quality of the liquid, however limpid the solution may be, producing an effect which may be compared to opalescence or turbidity in a liquid employed in the transmission of luminous rays.

11. I have not been able to trace any special connexion between the chemical complexity of a substance and its diactinic power. Carbon in its pure form as diamond we regard as an element. In thin slices it transmits portions of the chemical rays of nearly all degrees of refrangibility, though none of the specimens which I examined exhibited any approach to the actinic limpidity of quartz. Phosphorus, on the other hand, though transparent to light in its melted condition, and equally regarded as elementary, appears to be nearly *adiactinic,* or impermeable to the chemical rays. In many cases the peculiar diactinic or adiactinic action of an element is traceable in its simpler chemical compounds. Thus the simpler combinations of sulphur, such as sulphuretted hydrogen, sulphurous acid gas, bisulphide of carbon, and chloride of sulphur, are all powerful actinic absorbents, while in the more complicated form of sulphuric acid and the sulphates of certain bases, the compounds are highly diactinic. On the other hand, the silicates are much less diactinic than silica in the form of quartz, or the bases which

enter into the formation of the silicates; probably this may arise, as Professor Stokes suggests, from the difficulty of obtaining silicates, either natural or artificial, after fusion, perfectly free from iron.

12. No solid or liquid substance that I have as yet tried, surpasses rock-crystal in permeability to the rays which excite chemical action. Ice (and water), as well as white fluor-spar, rival it; and pure rock-salt approaches it very closely.* White topaz is a little inferior to the preceding bodies in diactinic capacity.

Amongst the various compounds submitted to examination, the *fluorides* rank first in diactinic power; then follow the *chlorides* of the metals of the alkaline earths. The *bromides* of the same metals appear to be less diactinic than the fluorides and chlorides, and this decline in power is still more marked in the case of the *iodides*. The short spectrum of these last-mentioned salts is interrupted by a well-marked absorption-band at a point beyond H, represented on the arbitrary scale at 103·5, beyond which the spectrum is again faintly renewed to 113·5, and then it terminates abruptly. The *cyanides* appear to be considerably diactinic; but further experiments upon these salts, as well as upon the *sulphocyanides*, are desirable. *Sulphuric, carbonic,* and *boracic* acids furnish salts with the alkalies and alkaline earths, which are also largely diactinic; the *phosphates* seem to be less so, and the *arseniates* still less. It is remarkable, that though the sulphates are so diactinic, the *sulphites* are considerably less so, and the *hyposulphites* are more opaque than the sulphites. The *hydrates* of the alkaline earths are also transparent. It is very difficult to obtain the alkaline hydrates perfectly pure; but a solution of hydrate of soda and one of potash, obtained by precipitation of their respective sulphates with baryta, and concentrated in a silver dish, gave a very fair result in each case.

The diactinic capacity of the *tartrates* and *citrates* is less than that of the carbonates. That of the *acetates* appears to be about the same as that of the tartrates; but the results obtained with the acetates are somewhat uncertain, as it is difficult to procure these salts absolutely free from the empyreumatic products which accompany the acid as it is usually prepared. The *oxalates* have a low diactinic power.

---

* A specimen of sea-water which had been standing for some months in my laboratory, furnished a result identical with that obtained by using a strong solution of pure chloride of sodium.

and the lengths of the different spectra, in terms of the scale already explained (par. 7). The compounds included in the preceding Table, with the exception of nitric and hydrochloric acids, are not simply solutions, but liquids to which a definite chemical formula may be assigned.

The starting-point for each spectrum was 96·5 upon the scale already adopted.

Of all these liquids, water and alcohol are the only two, except sulphuric and hydrochloric acids, which are strongly diactinic; water is eminently so, alcohol in a much less degree. No relation in this respect is traceable between common alcohol and the other alcohols examined, viz.: wood-spirit, fousel oil, glycol, glycerin, and the phenic alcohol, carbolic acid. Bisulphide of carbon, the refractive medium employed in my earlier experiments, is singularly deficient in diactinic power, and is therefore eminently unfit for such researches.

### c. *Absorption of Chemical Rays by transmission through Gases and Vapours.*

17. In the experiments upon the absorbent action of aeriform media, the gas or vapour under trial was introduced into a brass tube two feet long, blackened on the inside, and closed at the end by plates of quartz, which were fitted on so as to form air-tight joints. The tube could be attached by a stopcock to the plate of the air-pump, and after exhausting the air, any gas could be easily introduced. In cases in which the gas was liable to act upon the metal, a glass tube was substituted for the metallic one, and the gas was introduced by displacement. The tube when prepared was interposed at *t*, fig. 1 (par. 6), between the slit *s* and the prism *b*, and the rays emanating from the electric spark were, after traversing the column of gas contained in the tube, received first upon the prism and lens, and then upon the excited collodion surface, in the usual manner.

When the vapour of a volatile liquid was to be examined, a few drops of it were generally allowed to fall into the tube filled with air, through which the vapour was allowed to diffuse itself at the ordinary temperature. The action of such vapours was therefore compared at a great disadvantage with that of the various gases, particularly where the volatility of the liquid was rather low. The results, however, even under these disadvantageous circumstances, were well marked, as may be seen by examining the subjoined Table of gases and vapours submitted to experiment, in which the comparative lengths of the different spectra are shown in the second column of figures.

Table III.—*Absorbent action of Gases and Vapours on the Chemical Rays.*

Length of column of gas 2 feet.

| Name of Gas. | Termination of spectrum. | Relative lengths of spectra. | Remarks. |
|---|---|---|---|
| Atmospheric air | 170·5 | 74·0 | |
| Hydrogen | 170·5 | 74·0 | |
| Carbonic acid | 170·5 | 74·0 | |
| Carbonic oxide | 170·5 | 74·0 | |
| Olefiant gas | 162·5 | 66·0 | |
| Marsh-gas | 159·5 | 63·0 | |
| Coal-gas | 133·5 | 37·0 | Cut off abruptly. |
| Protoxide of nitrogen | 159·5 | 63·0 | |
| Cyanogen | 159·5 | 63·0 | |
| Ammonia | 170·5 | 74·0 | |
| Sulphurous acid | 110·5 | 14·0 | Cut off abruptly. |
| Sulphuretted hydrogen | 110·5 | 14·0 | Cut off abruptly. |
| Bisulphide of carbon | 101·5 | 6·0 | A few of the strongest lines between 140 and 152 are seen. |
| Dichloride of sulphur | 108·0 | 10·0 | |
| Benzol | 131·5 | 35·0 | Faint beyond 111·5. |
| Oil of turpentine | 152·0 | 55·5 | |
| Chloroform | 152·0 | 55·5 | |
| Ether | 163·5 | 67·0 | |
| Terchloride of phosphorus | 131·5 | 35·0 | Very feeble spectrum. |
| Oxychloride of phosphorus | 141·5 | 45·0 | Fades out very gradually. |
| Hydrochloric acid | 151·5 | 55·0 | |
| Hybrobromic acid | 119·5 | 23·0 | Cut off abruptly. |
| Hydriodic acid | 111·5 | 15·0 | Cut off abruptly. |
| Peroxide of nitrogen | 0 | 0 | |
| Peroxide of chlorine | 0 | 0 | |

18. The absorbent action disclosed by the foregoing experiments on the colourless gases and vapours is very interesting, as it proves that differences exist in the diactinic power of these substances quite as marked as in the case of liquids and solids. Some of the *elementary* gases—oxygen, hydrogen, and nitrogen—appear to possess a diactinic capacity greater than any solid or liquid body. Many *compound* gases, such as ammonia, carbonic acid, and carbonic oxide, appear to rival them. Olefiant gas, cyanogen, and

hydrochloric acid exhibit a decided but not great absorptive power, with which that of the vapours of ether, chloroform, and oil of turpentine at the atmospheric tension, and when diffused through air, may be compared. Doubtless if these vapours were tried at a tension of 30 inches, they would exhibit greater absorptive power. The absorptive action of hydrobromic acid much exceeds that of the hydrochloric, and that of hydriodic acid is greater than of either.

The abrupt termination of the spectrum in coal-gas is remarkable. The absorption appears to be due, not to the permanent gases, but to the vapours of benzol and other heavy hydrocarbons which it contains. The four compounds of sulphur, viz.: sulphurous acid,* sulphuretted hydrogen, bisulphide of carbon, and dichloride of sulphur, are especially active in absorbing the chemical rays; and the vapours of the terchloride and oxychloride of phosphorus exhibit a similar though less intense absorptive power.

19. Coloured gases, whether elementary or compound, such as chlorine, bromine, and nitrous gas, have long been known to exert an absorptive action upon the luminous rays;† and their effect is not less marked upon the invisible prolongation of the electric spectrum.

The effects of the three halogens, chlorine, bromine, and iodine, in the form of vapour, are particularly remarkable. As a general rule, when a body exerts an absorptive influence, the absorption is greatest in the most refrangible portions; but the reverse of this occurs in the case of chlorine and of bromine. A column of *chlorine* two feet in depth, cuts off the whole of the *less* refrangible portion as far as 143·5; beyond that a distinct impression is obtained as far as about 159. With *bromine* diffused in the form of diluted vapour, the impression commences at 106, and is continued distinct, though rather feeble, to the extreme end of the spectrum. The apparatus required a slight modification to adapt it for the experiment with *iodine*. I used a glass tube six inches long, the open ends of which were ground flat so as to admit of being closed by thin plates of quartz; this was enclosed in a brass tube; a few grains of iodine were introduced, and the quartz plates fixed by metallic caps perforated to admit the passage of the rays; this tube could then be supported as usual between the spark and the prism, and could be raised to and kept at a temperature beyond that necessary for the volatilization of the iodine. The electric light, after traversing such a column of vapour of an intensely deep violet colour, gave a strong spectrum, extending from 96·5 as far as 112, then it gradually faded till it disappeared at about 118; the impression became again rather faintly but distinctly visible at 142, and gradually disappeared at about 156. It is interesting to notice a somewhat similar interrupted absorption of the rays, though at a different part of the spectrum, in the case of the metallic iodides.

---

* An aqueous solution of sulphurous acid cuts off the spectrum at the same point as the gas itself does.

† For an historical sketch of the progress of discovery in relation to the production of bands in the spectrum, the reader is referred to a paper by the author in the "Pharmaceutical Journal," February, 1862, p. 17, *et seq.*

Both peroxide of nitrogen and peroxide of chlorine, in a stratum of two feet in depth, wholly absorb the chemical rays; but when more dilute or in shorter columns, they each give characteristic absorption-bands.

20. There appears to be little or no connexion between the absorptive power of any particular gas for the chemical rays, and its power of absorbing radiant heat as determined by the experiments of Dr. Tyndall.* Aqueous vapour is highly diactinic, though not diathermic: olefiant gas exhibits a similar difference: and various other instances might be pointed out.

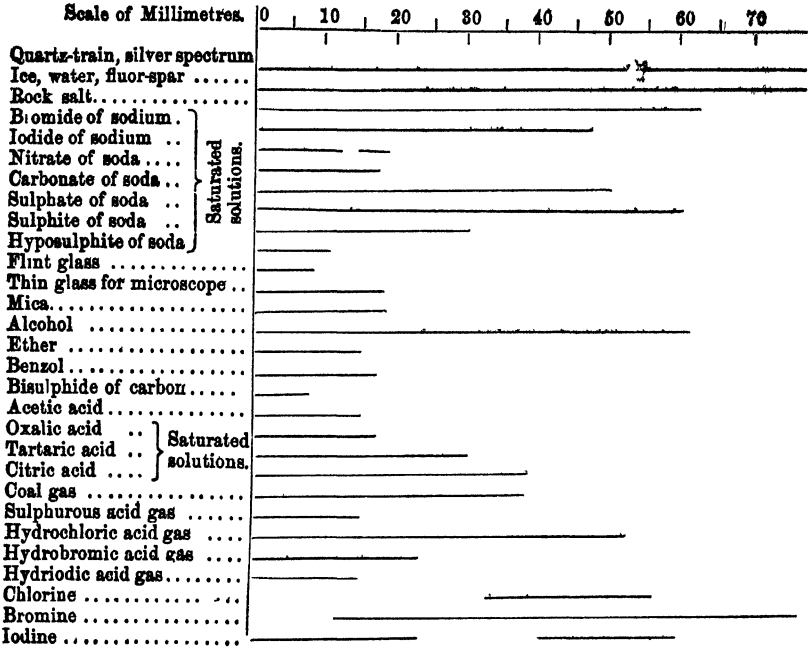
21. The most interesting fact, however, disclosed by these various experiments is the persistence of either the diactinic or the absorbent property in the compound, whatever be its physical state—a circumstance which proves that the property under consideration is intimately connected with the atomic or chemical nature of the body, and not merely with its state of aggregation.

The following diagram represents approximatively the relative position of the portions of the spectrum transmitted in a few of the cases described in the foregoing section of this paper. No attempt is made to indicate partial absorption of the rays. In one or two instances, where complete absorption at a particular part of the spectrum occurs, this has been indicated by an interruption in the line.

---

* Phil. Trans. 1861.

*Relative Absorptive Action of various Media upon the Electric Spectrum of Silver.*



## § 2. THE ABSORPTION OF THE CHEMICAL RAYS BY REFLEXION FROM POLISHED SURFACES.

22. In my earlier experiments I had much difficulty in obtaining a spectrum all the parts of which were even approximatively in focus in the same plane, and, with the view of remedying this defect, I tried the effect of substituting specular reflexion for the refracting action of a lens. This led me to compare the reflecting power of different polished surfaces for the chemical rays. With this object in view, a small polished plate of the material under experiment was supported at an angle of 45°, as shown in Fig. 3, (par. 6), opposite the vertical slit of the apparatus, so that when the source of light *e* was placed at right angles to the axis of the tube, the rays were reflected down the tube in the direction of that axis. The arrangement of the prism, lens, and camera was the same as that already described (6). As, however, much less light was reflected upon the prism from the polished surface than

that which fell upon the prism when the direct rays of the spark were employed, the exposure of the sensitive plate in the camera was prolonged from five minutes to ten.

23. Among the metals and alloys thus submitted to trial were platinum, gold, silver, mercury contained in a trough with quartz faces, lead, copper, tin, cadmium, zinc, aluminum, steel, brass, and speculum-metal. In addition to these, the reflecting-power of quartz, window-glass, and Iceland spar was also tried.

No judgment of the perfection of the reflecting-power could be formed from the colour of the metal. *Gold* possesses the power of reflecting all the rays, even the most refrangible, very equally, though somewhat feebly. Next to gold ranks burnished *lead*, some part of the spectrum of the electric spark reflected from lead being more intense than that from gold. The length of the spectrum obtained from the light of the electric spark between silver points, by reflexion from the surface of these two metals, extended from 96·5 to 170·5, or over the full distance of that obtained by the direct light of the spark, viz., 74 divisions of the scale which I have adopted. With all the other metals the spectrum of the same reflected spark terminated at 159·5, covering only 63 divisions of the scale.

The spectrum from a *silver* surface was remarkable. The impressed image was strong up to 112·5; then an abrupt cessation of the reflected rays occurred for a distance of 1·5 division; beyond this the reflexion gradually returned, and continued tolerably intense till it reached 159·5, covering 63 divisions of the scale.

The reflexion from *mercury* was weak in the middle, but strong towards each extremity. *Platinum, zinc,* and *aluminum* resembled mercury in their effects, but the spectrum was much less intense. The reflexion from *cadmium* was similar, but still weaker.

The spectrum of the rays reflected from *copper* was deficient in strength for the last half of the more refrangible portion; and that of *brass* was similar to it, but weaker. The reflexion from a surface of *steel* was more intense than that from any surface which I employed, but it ended abruptly at 159·5, or at the 63rd division of the scale. The spectrum reflected from *tin* was nearly as complete as that from steel.

A small concave mirror of *speculum-metal* gave an intense spectrum for the first half; but the more refrangible portion was deficient in power, and no rays were reflected beyond 159·5

(63 divisions), the point at which the other metals also failed. I therefore abandoned the attempt to substitute a speculum for the lens, with which latter I succeeded subsequently in obtaining a field sufficiently flat for the purpose.

24. The reflexion from the surface of transparent objects was so scanty that, of course, no idea was entertained of using such bodies as mirrors; but it may be worthy of notice that a feeble spectrum was obtained from surfaces of *quartz*, *window-glass*, and *Iceland spar*, extending to 159·5, or over a length of 63 divisions of the scale—that is to say, fully as far as the majority of the metals. The quantity of the reflected rays was small, but its quality was similar to that of the rays reflected from metallic surfaces.

## § 3. Photographic Effects of the Electric Spectra of different Metals taken in Air.

### a. *Pure Metals.*

25. I have spent a considerable time in endeavouring to procure exact photographs of these spectra, inasmuch as the spectrum of a metal is a constant not less important than its density or its fusing-point; and it frequently furnishes the means of identifying an element under circumstances in which no other method at present known is practicable.

Kirchhoff, in his elaborate and masterly researches on the constitution of the solar spectrum, has, as is well known, published in minute detail a map including the lines of a large number of the metals. He has, through a limited portion of the visible spectrum, laid down the position of the bright lines of certain metals coincident with particular dark lines of Fraunhofer, with a precision best appreciated by those who have followed him with most minuteness.

Much yet, however, remains to be done, even for the rays which fall within the range of the visible spectrum; and for those which are beyond the limits of ordinary vision, the whole yet remains to be examined.

The lines of each spectrum are so numerous and so close together, that it would be impossible, without a sacrifice of time that would scarcely be justifiable, to obtain accurate impressions of them by eye-drawing. Indeed, except by the process of photography, these lines can only be rendered visible by the aid of a fluorescent screen, under which circumstances the minute details are almost necessarily lost, even by the most careful observer.

The photographs of these spectra were obtained by an arrangement of the quartz prism and lens, identical with that already described (6), wires, plates, or irregular fragments of the metal, according to circumstances, being supported in brass forceps connected with the secondary wires of the induction-coil. The interval traversed by the spark was in each case about a quarter of an inch, and the slit was placed at a distance of half an inch from the line traversed by the spark.

The specimens of gold, silver, mercury, copper, bismuth, antimony, zinc, tellurium, thallium, and lithium employed, are believed to have been pure. The tungsten, molybdenum, chromium, and manganese were reduced from pure oxides in crucibles lined with charcoal. The other metals were as they are furnished in commerce as pure.

26. Each metal gives its own distinctive spectrum; but it is remarkable that these differences are not obvious in the less refrangible end. The true metallic spectrum, when the sparks pass in air, is in fact combined with that due to atmospheric air, as has already been pointed out for the visible rays by Ångström and by Alter. The photographic lines of the air-spectrum are most marked in the less refrangible portion, whilst the characteristic lines of the metals are particularly evident in the more refrangible parts. Hence the photographs which I formerly obtained by the use of a prism of bisulphide of carbon, which transmits rays of low refrangibility only, represent, as I then correctly pointed out, lines which are chiefly atmospheric; and consequently they exhibit appearances which are almost identical whatever be the metal employed.

In describing the spectra of the different metals, I shall employ the same arbitrary scale that I have hitherto used in this paper.

27. It will be observed that generally the lines, as they advance towards the more refrangible extremity, become less intense in their central portion, until, towards the extreme limit of the spectrum, the two marginal ends of the lines alone are visible, though these terminations are often rather intense. Indeed, throughout the whole length of the impressed photograph, the marginal extremities of the metallic lines leave a stronger image than their central portions, as though the incandescence of the volatilized portions of the electrodes, owing to their high radiating

power, did not continue sufficiently intense during their transfer across the interval between the two electrodes, to enable them to produce a continuous line. Evidently the cause of this diminution of action operates more powerfully upon the more refrangible rays; and a higher temperature, as the experiments of other observers have abundantly proved, is necessary to the production of radiations of these high degrees of refrangibility.

Exceptions to this remark occur in the lines due to the atmosphere; this is well seen in the strong line at 110·5, which is in marked contrast to some of the metallic lines in its vicinity, particularly in the spectrum of silver (Plate XXXIX. Fig. 9), where this nitrogen-line is included between two pairs of very intense lines due to the metal itself, and which are each interrupted in the middle.

In order to abbreviate the description of the various spectra, I shall generally speak of these interrupted lines as "*dots*;" they, indeed, constitute the characteristic features of the different metallic spectra. These dots, if the image be exactly in focus, may usually be seen to consist of groups of very short lines closely aggregated. This is well shown in some parts of Plate XL. Fig. 39, which represents the spectrum of silver; and it is less distinctly shown in the spectra of palladium (Fig. 38), of copper (Fig. 40), of antimony (Fig. 41), and of cadmium (Fig. 42). These spectra were taken with the screen, lens, and prism at a distance from the slit, different from those with which the other impressions were procured; some parts are consequently out of focus, but the details of other portions are shown more fully.

As might be anticipated, the spectra of the more volatile metals are the most intense—those of bismuth and antimony, of cadmium, zinc, and magnesium being especially remarkable in this respect.

A certain similarity is also observable in the spectra of allied metals, as in the case of the three metals last mentioned, also in those of iron, cobalt, and nickel, of bismuth and antimony, as well as of chromium and manganese.

It should further be observed that, in estimating the apparent length of the different spectra, considerable difficulty is frequently experienced, owing to the extremely faint impressions which the most refrangible rays commonly occasion; in some experiments, this portion of the spectrum with the same metal appears to be longer than in others made under apparently similar conditions.

The strongly marked character of the spectrum of silver, and particularly the renewal of its intensity towards the more refrangible end, rendered it very appropriate for the purpose of testing the diactinic quality of different media; and accordingly I have used it more extensively than any other metal in the experiments already detailed upon this subject. (Plate XXXIX. Fig. 9, and Plate XL. Fig. 39.)

*Thallium.*—The spectrum of thallium (for a specimen of which in a pure state I am indebted to the kindness of Mr. Crookes, its discoverer) is particularly interesting, as in its visible portion it is remarkably simple, the single intense green line being the only one visible, even when heated in the intense flame of the oxyhydrogen jet. When, however, the sparks of the secondary coil are transmitted, not only do new lines make their appearance in the visible spectrum, but also in the extra-violet portion, and the complex impression shown at Plate XL. Fig. 45 is developed. This character of its spectrum* separates thallium from the metals of the alkalies. In the less refrangible portion are two strong groups of lines at about 103 and 106; three other groups occur at 116, 121, and 126 respectively, the two first less intense, the third of about the same strength as the first pair of groups. Several feebler pairs of dots follow; and the spectrum terminates with four nearly equidistant groups, commencing respectively at 136, 141, 145, and 151: the first of these groups is very strongly marked, the others are fainter but of nearly equal intensity.

*Mercury.*—Experiments were made with this metal by soldering a platinum wire into a small glass tube which was filled with mercury and connected by means of the platinum wire with one end of the secondary wire of the coil; the other electrode consisted of a platinum wire. The spectrum obtained exhibited few lines, excepting those due to the mercurial electrode. The never-failing nitrogen line, 110·5, was evident; but there were numerous strong lines due to the mercury, the most distinct of which are those at 104, 114·5, 117·5, 119·0, 122·5, 131·0, 138, 156, 159, each of the two last forming a strong broad group of dots, the last group terminating the spectrum at 161·0. (Plate XXXIX. Fig. 10.)

*Magnesium.*—This is another remarkable spectrum. An intense group of lines commences at 101; at 115 a bright group of dots is seen, and between 119 and 126·5 are three remarkably intense groups of lines: the first of these comprises at least four strong lines, the second group three, and the third consists of eight or ten separate lines. This last is the most intense group that I have met with in the course of these experiments. Beyond this the spectrum is prolonged by a faint tail, which is strongest along the edges, and nearly vanishes midway between them; this tail disappears a little beyond 150. (Fig. 28.)

---

* Proceedings of the Royal Society, January, 1863, vol. xii, p. 407.

56. It is unnecessary to give any details of experiments made with electrodes one of which consisted of one metal and the other of a different metal. Under these circumstances, the lines starting from the side corresponding to each metal are identical with those furnished by the particular metal. This mode of making the experiment is therefore frequently convenient when it is desirable to compare the spectrum of any given metal with another selected for comparison. When the difference in volatility between the two is extreme, as when platinum is opposed to mercury (Fig. 10), it may happen that one spectrum only is seen, the lines starting from one edge of the photographic impression, and terminating at irregular distances before they reach the opposite edge.

## b. *Spectra of Alloys.*

57. The principal object of these experiments was to determine the influence which small amounts of foreign metals exercise upon the photographic image. When equal weights of the two metals are employed (tin and lead, for example, or cadmium and lead), a compound spectrum exhibiting the lines due to both metals is produced; and it is not always the more volatile metal that predominates. An alloy containing 62 parts of copper and 38 of zinc, gave a spectrum in which the lines due to copper predominated considerably. In an alloy of about 2 parts of zinc to 1 of cadmium the zinc-spectrum was the most strongly marked.

In another experiment, an alloy of 990 parts of fine gold and 10 of fine silver was prepared; on taking the spectrum obtained by an exposure of 10 minutes, a distinct but feeble impression of the more refrangible lines due to silver was procured (see Fig. 8). A contamination of gold with silver to an extent not exceeding 1 per cent. could therefore be recognized by this means; but prolonged exposure was necessary in order to develope the lines due to silver. An analogous result was obtained when the spectrum of plumbago was taken. In this case, in addition to the atmospheric lines, the spectrum of iron was distinctly impressed; the total amount of metallic iron in the plumbago was 3·94 per cent. Graphite deposited in the gas-retorts, which contained 0·23 per cent. of iron, gave very feeble indications of iron. On the other hand, no indication of iron was observable in the spectrum of brass which contained 0·23 per cent. of iron, nor was lead indicated in brass which contained 0·7 per cent. of this metal.

58. All the foregoing spectra were obtained either from the metals in their uncombined form, or else from their alloys. The electric spectra of a few other metals which admit of being submitted to experiment in their isolated form, still remain to be added. A considerable proportion of the metallic elements, however, are not included in the foregoing list. These it is almost impossible to examine, except in the form of some of their saline or other compounds. As, however, this portion of the inquiry is attended with some peculiar difficulties, I shall defer what I have to add upon this subdivision of the subject to a future occasion.

### § 4. PHOTOGRAPHIC EFFECTS OF ELECTRIC SPECTRA OF DIFFERENT METALS PRODUCED BY TRANSMITTING THE SPARKS THROUGH GASES OTHER THAN ATMOSPHERIC AIR.

59. In making experiments upon the influence of various gases upon the spectra of the electric spark, the arrangement of the apparatus was modified in the following manner:—The position of the slit, prism, lens, and camera, was the same as in the preceding experiments (6); but the metallic electrodes were enclosed in a stout glass tube, shown at half its real size in Plate XL., Fig. 49. *a* is the tube itself, *b* a hole drilled through the side of the tube, which upon this side is ground flat in order that it may be closed air-tight by the thin plate of polished quartz *c*. This plate is kept in its place by means of an elastic band. *d*, *d* are brass forceps screwed into the brass plugs *e*, *e*, for holding the electrodes. The ends of the tube are closed by the brass plugs *e*, *e*, which are ground to fit the ends of the tube, and are pierced by small brass tubes for the conveyance of the gas. An elastic band, passing from one end of the glass tube to the other, keeps the brass plugs in their place. The tube is then connected with a gas-holder filled with the gas under experiment (or, when practicable, the gas is disengaged during the experiment), and, after the apparatus has been connected with the induction-coil and adjusted in its proper

position, a slow current of the gas at the atmospheric pressure is transmitted, the excess of gas, as it passes out of the apparatus, being conveyed into the chimney or out of the window by a suitable arrangement of tubes.

A simpler apparatus was admissible when the wires could, like those of platinum or of iron, be soldered into glass. Fig. 50 shows this modification. A piece of tubing *a*, about an inch and a half long and half an inch in internal diameter, is united at each extremity to a piece of quill tubing *e, e;* the wires *d, d* are then soldered through its sides. A portion of the wide tube is ground away as at *b*, leaving an opening to which the quartz plate *c* can be applied, and kept in its place by small rings of caoutchouc. The gas was transmitted through the tube as in the other form of apparatus.

60. In one or other of these modes, the following gases were submitted to experiment:—hydrogen, carbonic acid, carbonic oxide, olefiant gas, marsh-gas, cyanogen, sulphurous acid, sulphuretted hydrogen, ammonia, protoxide of nitrogen, nitrogen, oxygen, chlorine, and hydrochloric acid.

The general results of these experiments on the invisible rays are in harmony with those already obtained for the visible ones by MM. Ångström,* Alter,† and Plücker.‡ The conclusions at which I have arrived may be thus summed up:

1. Each gas tinges the spark of a characteristic colour; but no judgment can be formed from this colour of the kind of spectrum which the gas will furnish.

2. In most cases, in addition to the lines peculiar to the metal used as electrodes, new and special lines characteristic of the gas, if elementary, or of its constituents, if compound, are produced. When compound gases are employed, the special lines produced are not due to the compound as a whole, but to its constituents.

3. The lines due to the gaseous medium are continuous, not interrupted or broken into dots.

61. *Hydrogen.*—The spectrum of the spark taken in this gas is not characterized by any new lines. The most remarkable effect is the disappearance of the atmospheric lines, together with the great lowering of the photographic intensity, whether the metal employed be platinum, gold, silver, copper, iron, or zinc. It is

---

* Pogg. Ann., 1855, xciv, 141.

† Pogg. Ann., 1859, cvii, 497.

‡ Silliman's Journal, 1855, xix, 213.

interesting to observe, that the characteristic lines of highly oxidizable metals, such as iron and zinc, are visible in hydrogen, though the impression on the plate throughout is very greatly reduced in intensity.

62. *Carbonic Acid and Carbonic Oxide.*—The lines contained in the spectra of these two gases are identical; new lines characteristic of carbon occur in addition to the lines due to the nature of the metallic electrodes. The same lines are visible when other compounds of carbon, such as olefiant gas, marsh-gas, and cyanogen, are employed. The most characteristic lines in the spectrum of carbon are the following:—At 123 a strong line, a weaker one at 127, two strong compound lines at 138 and 140, and an intense compound line at 153.

With carbonic acid the special spectrum of silver appears much intensified. Some of the lines which appeared as dots in air are continued across the spectrum in carbonic acid. In carbonic oxide the intensity of the spectrum is less than in air; and this contrast between the two gases may be observed whatever be the nature of the metallic electrodes.

Fig. 35 exhibits the spectrum obtained between platinum points in carbonic acid. Fig. 36 shows the spectrum from gold points in carbonic oxide. Unfortunately, in the plate the figure is given a little too much to the right of its true position for accurate comparison with the spectrum above it; but the principal lines will at once be recognized as coinciding, if allowance be made for this displacement.

63. *Olefiant gas.*—Some difficulty is experienced in observing the spectrum of this gas, owing to the copious deposition of carbon which occurs immediately that a current of sparks is transmitted. The nature of the electrodes employed seems to exert considerable influence upon this decomposition. It is extremely intense when aluminum electrodes are used, but comparatively slight with gold. Observations made when gold electrodes were employed exhibited a spectrum which could not be distinguished from that of carbonic acid or of carbonic oxide.

64. *Marsh-gas.*—Sparks pass freely in this gas. The spectra obtained with gold and copper electrodes cannot be distinguished from those of the same metals in carbonic acid and carbonic oxide. A scanty separation of carbon occurs during the passage of the spark. This is particularly evident when copper electrodes are used, the bluish light of the metallic spark being frequently

accompanied by reddish-yellow scintillations; the deposition of finely divided carbon upon the quartz plate on the side of the gas-tube impairs the intensity of the photograph.

65. *Cyanogen.*—A difficulty was experienced in this case also in obtaining intense photographs, particularly when silver electrodes were employed; a rapid deposition of a brown matter, probably paracyanogen, took place upon the interior of the tube. When copper electrodes were used, the light of the spark was sometimes of an intense green, at others of a pale blue. The photograph showed the particular lines due to carbon as well as those of nitrogen, and the special lines due to the metallic electrode employed.

66. *Sulphurous Acid.*—This gas offers unusual resistance to the passage of the electric sparks, the electrodes requiring to be brought very close to each other before the disruptive discharge passed freely. This difference in the power of different gases to modify the striking distance has already been examined by Dr. Faraday.* A strong spectrum was obtained with gold wires; it terminated abruptly at 113·5, a single spot of renewed action appearing at 143·0. This result is due, no doubt, to the absorbent action of the gas, which has been already shown, in a former section of this paper (18), to be one of the least diactinic of gaseous bodies. In this form of experiment the stratum of gas traversed by the rays before they entered the air, amounted to about half an inch in thickness.

67. *Sulphuretted Hydrogen.*—This gas also offers considerable resistance to the passage of the electric spark. It is decomposed by the spark with deposition of sulphur. When gold electrodes are used, it furnishes lines resembling those of the same metal in air. With silver electrodes the gas was decomposed very rapidly, and no lines were produced beyond 113·5, the absorbent action of the gas being strongly manifested.

68. *Ammonia.*—Sparks pass in this gas as freely as in air; the spectrum of each metal is the same as in nitrogen; no new lines are visible in the photograph. Most of the atmospheric lines are distinct.

69. *Protoxide of Nitrogen.*—The electric sparks pass in this gas with much greater difficulty than in air. The spectrum appears to be the same as that produced in air, and no new lines are apparent in the photograph.

---

* Philosophical Transactions, 1838, p. 103.

70. *Nitrogen.*—The spectrum of this gas, when gold or platinum electrodes are used, commences with a pale continuous spectrum, which slowly diminishes in intensity; this continuous spectrum appears to increase in intensity with the volatility of the metal, being well marked in the case of magnesium, sodium, and potassium; at about 151 it terminates abruptly. The spectrum of nitrogen is crossed between 96·5 and 100 by two strong double lines; it shows an indistinct line at 108·5, a strong one at 110·5, three feeble lines at 113·5, 118, and 122, a faint band at 138, and another at 150. Fig. 33 shows the lines obtained from platinum points in nitrogen.

71. *Oxyyen.*—This gas was obtained from black oxide of manganese heated with sulphuric acid. It gave, after purification by passing through a solution of caustic soda, lines identical with many of those obtained in atmospheric air. When the gas contained traces of carbonic acid, the lines due to the compounds of carbon were distinctly visible in the impressed spectrum. With platinum electrodes and with pure oxygen, a feeble, nearly continuous spectrum extends to about 122·5; it also contains numerous lines extending as far as 142·5; beyond that, the impression is more feeble, terminating at about 156. The principal lines due to the gas are the following:—A broad line about 100, then two faint lines, beyond which, at 101·5, is a double line; a strong complex group at 103·5; a feebler one at 105·5; one rather stronger at 107·5; a double group of considerable strength at 112; another stronger at 114; between 116 and 119 is a group of six rather faint lines; after this there are no prominent lines until 138·2 and 141·5; at 153 is a strong compound line, and beyond this only the dotted lines of platinum are seen. (Fig. 32.)

72. *Chlorine* and *Hydrochloric Acid* give spectra which can scarcely be distinguished one from the other. With platinum points these spectra terminate by an abrupt band at 156·5. Their most marked features are a strong compound band at 96·5, and one still more marked at 100; then two lines, of which the first at 103 is the stronger, followed by two others, of which the second at 108·5 is the stronger; several fainter lines follow these lines. A group of six between 126 and 133, the most marked of which is a broad band terminating at about 130. Several faint lines intervene between this and another broad band at 140, followed by several others less distinctly defined. (Fig. 34.)

I attempted to obtain the spectra of iodine and bromine by employing a current of hydriodic and hydrobromic acid; but the results were not satisfactory. It is very difficult to maintain a steady current of sparks through these gases, and not easy to keep up a continuous current of the pure and dry gases, which are immediately decomposed by the passage of the electric spark, with extrication of dense fumes of iodine or of bromine.

## X.—*On the Absorption of Mixed Gases in Water.*

### By Wm. M. Watts, B. Sc.

[Dalton Scholar in the Laboratory of Owens College, Manchester.]

In his memorable essay on the Constitution of Mixed Gases,* Dalton first propounded the idea that different gases afford no resistance to each others' particles, but expand freely into one another, as each would do into a vacuum.

Dalton appears to have been led to this conclusion, solely from a consideration of the homogeneous nature of the atmosphere (Cavendish, 1788), and from the fact that when two gases of different densities are mixed, the heavier does not separate from the lighter by virtue of the attraction of gravitation.

That gases act in all respects as vacua to each other can scarcely be maintained; but that two permanent gases when mixed are, as regards pressure, in the condition expressed by Dalton's law, has long been generally admitted. One of the most striking proofs of the truth of this theory of mixed gases is afforded by the fact, that the diminution of solubility of certain gases in water is proportional to the reduction of pressure, whether that reduction be effected by allowing the gas to occupy a larger volume, or by mixing it with a corresponding volume of another gas.

The accurate experimental proof of the truth of this law was thus first given by Professor Bunsen,† in the case of mixtures of carbonic acid and carbonic oxide, and of carbonic oxide and marsh gas; inasmuch as it was shown that the quantities of the gases absorbed in water from these mixtures were in exact accordance with the quantities calculated from the several co-efficients of absorption on the assumption of the truth of this law.*

---

* Dalton, Manchester Memoirs, vol. v.

† Bunsen's Gasometry, p. 176.

Professor Roscoe* has since shown that mixtures of certain gases—chlorine with hydrogen, and chlorine with carbonic acid—do not conform to this law, inasmuch as the quantity of chlorine which dissolves in water from these mixtures differs from that quantity which would have been dissolved if the pressure had been altered by simply increasing the volume to a corresponding extent. This deviation from the law of absorption may be referred, either to a molecular resistance which the particles of these gases offer to each other, thus forming an exception to the law of partial pressures, similar to that found by Regnault† in the case of the vapours of water, ether, benzine, &c., or it may be caused by certain attractions occurring in the solution sufficient to disturb the absorptiometric equilibrium, as in the case of the absorption of hydrochloric acid in water,‡ or of carbonic acid in solutions of phosphate of soda.§

For the purpose of obtaining evidence as to the probability of one or other of these explanations, it appeared of interest to examine the relations exhibited by the absorption in water of very soluble and easily condensable gases, such as ammonia and sulphurous acid, when mixed with other less soluble gases. The absorptiometric relations of these two gases for water have already been accurately determined. Sulphurous acid has been examined by Mr. Sims,‖ and ammonia by Messrs. Roscoe and Dittmar,¶ and also by Mr. Sims.** Their experiments showed that, under variations of direct pressure, extending from 30mm. to 2000mm. of mercury, these gases do not obey Dalton and Henry's law of absorption, at temperatures below 50°C. in the case of sulphurous acid, and 100°C. in the case of ammonia.

The following contains a description of the results of direct determinations of the solubility of ammonia and sulphurous acid in water, under variation of pressure caused by mixture with other gases.

---

* Chem. Soc. Qu. J., viii., 14.

† Ann. Ch. Phys., [3], xv.; Comptes rendus, xxxix., 345.

‡ Chem. Soc. Qu. J., xii., 128.

§ Ann. Ch. Pharm., Supplement band, ii, 157.

‖ Chem. Soc. Qu. J., xiv., 1.

¶ Chem. Soc. Qu. J., vol. xii. 128

** Chem. Soc. Qu. J., vol. 1.

## I. *Ammonia and Air in Water.*

The method adopted to determine the amount of ammonia dissolved by water in mixtures with air of various composition, was essentially that employed by Roscoe and Dittmar,* and again by Mr. Sims, in similar determinations. A mixture of ammonia and air was made in a large India-rubber gas-bag, holding about 5 cubic feet, which had been previously well dried. The ammonia was prepared by heating in an iron vessel powdered chloride of ammonium (dried at 100°C.), and finely powdered anhydrous lime which had been previously heated to redness. The ammonia evolved was passed through a long drying-tube filled with fragments of quicklime into the bag, which was then filled up with air dried by passing through two sulphuric acid wash-bottles and a large chloride of calcium tube.

At the commencement of the experiment, samples of the gas were collected for analysis over mercury in two long absorption tubes. The mercury used for this purpose was heated to 100°C., and the absorption tubes were carefully dried before each experiment. The volume of the mixture was then read off, the barometer and thermometer being noted, and the ammonia was absorbed by a coke ball moistened with sulphuric acid, the volume of the residual air saturated with aqueous vapour being again read off. The accuracy of this method of analysis is seen from the following example—one of the numerous experiments made for the purpose of testing the method:—

| No. 1. | Vol. | Press. | Temp. | Vol. at 0°C. 760 mm. |
|---|---|---|---|---|
| Volume of gaseous mixture employed ............ | 303·47 | 764·6 | 13° C. | 291·44 |
| After absorption of ammonia................ | 268·1 | 718·5 | 14° C. | 241·12 |

| No. 2. | | | | |
|---|---|---|---|---|
| Volume of gaseous mixture employed ............ | 330·4 | 759·5 | 13° C. | 315·19 |
| After absorption of ammonia................ | 288·32 | 722·4 | 14° C. | 260·7 |

Hence we have the percentage composition of the gas:

---

* Chem. Soc. Qu. J., vol. xii, 128.

| | No. 1. | No. 2. |
|---|---|---|
| Ammonia.......... | 17·268 | 17·287 |
| Air .............. | 82·732 | 82·713 |
| | 100·000 | 100·000 |

The absorption of the mixture of air and ammonia was effected in about 6 grm. of water placed in a bulb apparatus similar to that used by Sims (and represented in Fig. 3 of his paper), the weight and volume of which had been previously determined.

After the gas had passed through for a certain time, depending on the circumstances of the experiment, during which experience had shown that the liquid had become saturated, the bulb was sealed before the blowpipe—the height of the barometer at the time of sealing being observed.

The bulb and ends were then weighed together, and the barometer and thermometer at the time of weighing again observed. The bulb was then carefully broken under a known volume of standard hydrochloric acid, the whole of the liquid and contained gases being expelled by heating the bulb, and the amount of unneutralised acid determined by the addition of standard soda.

From the data thus obtained, the amount of ammonia absorbed by 1 grm. water, under the circumstances of the experiment, can be found.

The data employed in an actual experiment are given to illustrate the mode of calculation.

| | |
|---|---|
| Weight of bulb-apparatus, empty.............. | 22·7292 grm. |
| Capacity of apparatus to point of sealing ...... | 24·2 cb.c. |
| Weight of bulb and contents at 754·7 mm. and 11°C. | 29·2490 grm. |
| Barometer at closing ........................ | 764·1 mm. |

| | | |
|---|---|---|
| Composition of the gas by eudiometric analysis .. | Ammonia........ | 36·34 |
| | Air ............ | 63·66 |
| | | 100·00 |

Tension of aqueous vapour at 0° C. ........ 4·6 mm.

The bulb was broken under 150 cb.c. acid (1 cb.c. = 1·0038 × 0·0365 grm. HCl.), and required 24·1 cb.c. soda (1 cb.c. = 1·003 × 0·031 NaO) to neutralize it.

From this we find that the weight of the ammonia contained in the bulb is 2·1485 grm.

The bulb and contents weigh in air 29·2490.

The weight of the air displaced is 0·0299. The weight in vacuo of the bulb and contents is therefore 29·2490 + 0·0299 = 29·2789. The sp. gr. of the solution of ammonia being taken as 1, the volume of the contained liquid may be taken as 29·2789 — 22·7292 = 6·55 cb.c. The unabsorbed gas contained in the bulb, measured at 764·1 mm. and 0° C., is therefore 24·2 — 6·55 = 17·65, or at 0° C. and 760 mm., 17·74 cb.c., of which we find 6·4 are ammonia and 11·3 air.

| | |
|---|---|
| Now, 6·4 cc. ammonia weighs | 0·0049 |
| and 11·3 cc. air weighs | 0·0146 |

The total unabsorbed gas contained in the bulb weighs therefore 0·0195. The contents of the bulb weigh in vacuo 29·2789 — 22·7292 = 6·5497 grm. The weight of water and dissolved ammonia is therefore 6·5497 — 0·0195 = 6·5302 grm. The total ammonia found by analysis weighs 2·1485 grm. From this must be subtracted the weight of unabsorbed ammonia contained in the bulb at the time of sealing, viz., 0·0049. The weight of ammonia absorbed is therefore 2·1485 — 0·0049 = 2·1436 grm.

Hence we find that 6·5302 — 2·1436 = 4·3866 grm. water absorb 2·1436 grm. ammonia, or 1 grm. absorbs 0·489 grm. ammonia.

The pressure on the ammonia is 0·36337 × (764·1 — 4·6) = 276 mm. Under a direct pressure of 276 mm. 1 grm. water absorbs 0·491 grm. ammonia.

Two determinations at each particular pressure were made in order to confirm the results.

The determinations with ammonia and air have been made at two temperatures, viz., 20° C. and 0° C. In order to maintain the bulb at 20° C. it was immersed in a water-bath, provided with an arrangement by which the temperature could be kept to within $\frac{1}{10}$° C. of the required temperature. The thermometer used had been previously carefully compared with a standard thermometer from Kew.

For the temperature of 0° C. the bulb was immersed in a bath of finely powdered ice. In order to prevent the temperature of the bulb rising above 0° C. it was found necessary to cool the gas by passing it through a long double tube surrounded with ice before it entered the absorption bulb. Even then the results are true for 0·5° rather than for 0° C. It was likewise found absolutely necessary to pass the gas as it escaped from the bulb through two small wash-bulbs containing water, in order to prevent diffusion, which, without this precaution, invariably occurred.

One or two phenomena observed during the experiments are worth recording. The time required to saturate the water depends on the composition of the gas, a much longer time being required when the proportion of ammonia is small than when it is considerable. Thus, 2 hours was found sufficient to saturate water with a mixture containing 30 per cent. ammonia or more; with a mixture containing 17 per cent. 5 hours was necessary; while with a mixture containing 8 per cent., although the gas was passed through continuously for 9 hours, the liquid was not saturated. These differences were not observed in mixtures of sulphurous acid and carbonic acid.

The results of the experiments with ammonia and air are given in the following tables; for 20° C. in Table A, and for 0° C. in Table B. Column I gives the percentage of ammonia in the gas at the time of closing the bulb; II. the atmospheric pressure at the same time; III, the partial pressure on the ammonia as calculated from the numbers in I and II; IV, the weight of ammonia absorbed by 1 grm. water as observed; and V, subjoined for comparison, the amount of ammonia absorbed under the *direct* pressures of column III. These last numbers are taken, those for 20° C. from the paper of Mr. Sims, those for 0° C. from that of Messrs. Roscoe and Dittmar.

TABLE A.

*Ammonia and Air in Water at 20°. C.*

| I. | II. | III. | IV. | V. |
|---|---|---|---|---|
| 10·879 | 762·5 | 81 | 0·113 | 0·128 |
| 14·339 | 755·0 | 106 | 0·139 | 0·155 |
| 23·916 | 767·8 | 179 | 0·206 | 0·218 |
| 25·382 | 767·6 | 190 | 0·221 | 0·225 |
| 28·804 | 741·1 | 208 | 0·243 | 0·238 |
| 28·960 | 741·6 | 210 | 0·240 | 0·239 |
| 68·181 | 767·8 | 511 | 0·429 | 0·408 |

TABLE B.

*Ammonia and Air in Water at 0° C.*

| I. | II. | III. | IV. | V. |
|---|---|---|---|---|
| 7 893 | 768·8 | 60 | 0·161 | 0·197 |
| 9·414 | 766 2 | 72 | 0·202 | 0·221 |
| 15·734 | 753·7 | 118 | 0·293 | 0·308 |
| 16·772 | 771·6 | 129 | 0 302 | 0·320 |
| 17·277 | 771·4 | 132 | 0·321 | 0·325 |
| 19 621 | 777·9 | 137 | 0·329 | 0·332 |
| 20·666 | 740·8 | 144 | 0 349 | 0·343 |
| 22 185 | 759 0 | 167 | 0·366 | 0·372 |
| 36 337 | 764·1 | 276 | 0·489 | 0 491 |
| 36 647 | 764·1 | 278 | 0 490 | 0 493 |
| 55 535 | 752·3 | 415 | 0·611 | 0 619 |
| 56·095 | 752 8 | 420 | 0 619 | 0·622 |
| 69 905 | 765 1 | 532 | 0·695 | 0 716 |

FIG. 1

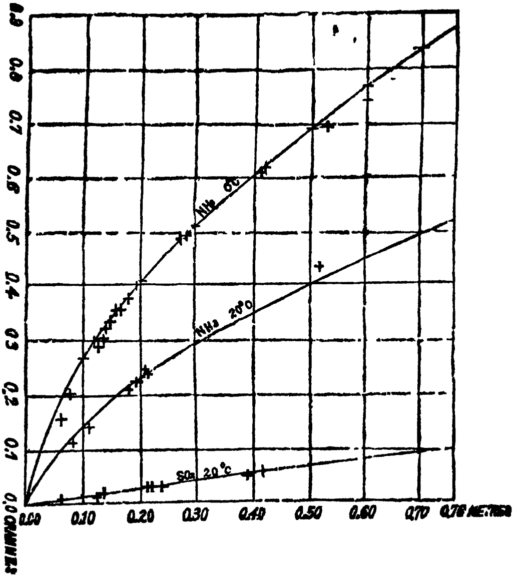


Fig. 1 gives graphical representations of the results embodied in these Tables. The line represents the curve of absorption under direct pressure, and the result of the experiments under partial pressure are marked by asterisks. It will thus be seen that, within the limits of experimental error, the amounts of ammonia dissolved when mixed with air, are the same as those absorbed under the corresponding direct pressures, but yet differ widely from those given by the simple law of Dalton and Henry. Hence we conclude that, in the case of ammonia, a deviation from Dalton's law of mixed gases, such as Regnault observed for the vapour of ether and other volatile bodies, does not become visible.

The co-efficients of absorption of ammonia are given in the following Tables. They are obtained by a careful interpolation from all the experiments,—those under directly-varied pressures (taken from the papers of Messrs. Roscoe and Dittmar, and of Mr. Sims), and those now obtained by reducing the pressure by mixture with air. They are given as being probably nearer approximations to the truth than those calculated from a more limited series of experiments. Table C contains the values for 0° C. Table D, those for 20° C. In both Tables column I contains the pressure in metres of mercury; column II the weight of ammonia, in grammes, absorbed by 1 gr. of distilled water under the corresponding pressures; and III the volume in cb. c., (measured at 760 mm. and 0° C.) absorbed by cc. water:—

TABLE C.

| I. | II. | III. | I. | II. | III. |
|---|---|---|---|---|---|
| m. | grm. | cb. c. | m. | grm. | cb. c. |
| 0·020 | 0·088 | 115·4 | 0·300 | 0·517 | 677·8 |
| 0·040 | 0·147 | 192·7 | 0·350 | 0·563 | 738·2 |
| 0·060 | 0·195 | 255·7 | 0·400 | 0·608 | 797·1 |
| 0·080 | 0·236 | 309·4 | 0·450 | 0·650 | 852·2 |
| 0·100 | 0·274 | 359·2 | 0·500 | 0·689 | 903·3 |
| 0·125 | 0·317 | 415·6 | 0·550 | 0·725 | 950·5 |
| 0·150 | 0·353 | 462·8 | 0·600 | 0·762 | 999·1 |
| 0·175 | 0·386 | 506·1 | 0·650 | 0·800 | 1048·9 |
| 0·200 | 0·413 | 541·5 | 0·700 | 0·835 | 1094·8 |
| 0·250 | 0·468 | 613·6 | 0·760 | 0·877 | 1149·8 |

TABLE D.

| I. | II. | III. | I. | II. | III. |
|---|---|---|---|---|---|
| m. | grm. | cb. c. | m. | grm. | cb. c. |
| 0·020 | 0·032 | 41·9 | 0·300 | 0·307 | 402·5 |
| 0·040 | 0·064 | 83·9 | 0·350 | 0·338 | 443·2 |
| 0·060 | 0·094 | 123·2 | 0·400 | 0·367 | 481·2 |
| 0·080 | 0·119 | 156·0 | 0·450 | 0·394 | 516·6 |
| 0·100 | 0·142 | 186·2 | 0·500 | 0·417 | 546·7 |
| 0·125 | 0·169 | 221·6 | 0·550 | 0·440 | 576·9 |
| 0·150 | 0·193 | 253·0 | 0·600 | 0·462 | 605·7 |
| 0·175 | 0·213 | 279·3 | 0·650 | 0·482 | 631·9 |
| 0·200 | 0·234 | 306·8 | 0·700 | 0·500 | 655·5 |
| 0·250 | 0·272 | 356·6 | 0·760 | 0·520 | 681·8 |

From experiments made with mixtures of ammonia and hydrogen, in the absorptiometer of Prof. Bunsen, Carius* came to the conclusion, that the former gas is absorbed in quantities directly proportional to the pressure.

Since these experiments were made, direct determinations, under considerable variations of pressure, have shown† that the above conclusion was incorrect, and that this gas does not obey Dalton and Henry's law. This discrepancy between the two statements arises from the fact, that the method of absorptiometric analysis cannot be employed for the purpose of ascertaining whether the gases in question obey the law. The general principle laid down by Bunsen is, that if the composition of the mixture employed, calculated from the absorptiometric experiment, coincides with that found by eudiometric analysis, we may conclude that the gases in question obey the law of absorption.

An examination of the formula,‡ employed to calculate the composition of the gaseous mixture from the data of the absorptiometric analysis, shows that, in mixtures of gases differing much in solubility, whilst the composition of the gas can be calculated with great accuracy when the co-efficients are given, the opposite course of calculating the co-efficients from the composition of the gas, does not yield exact results—the percentage-composition as calculated from the formula not being perceptibly affected by a considerable change in the co-efficient of absorption of either gas.

The formula referred to is the following :—

$$\frac{x}{x+y} = \frac{W-B}{A-B} \cdot \frac{A}{W}$$

$$\frac{y}{x+y} = \frac{A-W}{A-B} \cdot \frac{B}{W}$$

where

$$W = VP$$
$$A = (V_1 + \alpha h)P_1$$
$$B = (V_1 + \beta h)P_1.$$

In the unit-volume of the original gaseous mixture, there are $x$ volumes of the first gas, and $y$ volumes of the second.

$\alpha$ is the co-efficient of absorption of the first gas, and $\beta$ that of the second.

---

* Ann. Ch. Pharm. xcix. 129.

† Chem. Soc. Qu. J. xii., 147.

‡ Bunsen's Gasometry, p. 134, &c.

$V$ is the volume originally occupied by the gaseous mixture under the pressure $P$, and $V_1$ the volume of the unabsorbed gases at the pressure $P_1$.

Let $a$ be the co-efficient of the more soluble gas, so that $A$ is greater than $B$, and let $B = \kappa A$

Then, if $P_\beta$ stand for $\frac{y}{x+y}$, we have

$$P_\beta = \frac{\kappa A}{W} \frac{A - W}{(1 - \kappa)A}$$

$$\frac{\kappa}{1-\kappa} \cdot \frac{A - W}{W}$$

Suppose now that the co-efficient $a$ is increased, so that $A$ becomes $A + \delta A$,—then, if $P'_\beta$ be the new value of $\frac{x}{x+y}$,

$$P'_\beta = \frac{\kappa}{1 - \kappa} \cdot \frac{A - W + \delta A}{W}$$

$$\text{and } P'_\beta - P_\beta = \frac{\kappa}{1 - \kappa} \cdot \frac{\delta A}{W}$$

If $a = \beta$, so that $A = B$, we have (since $\kappa = 1$) an infinitely large change in percentage composition for any change in the value of $a$,—the nearer $\kappa$ is to unity, the larger is the change in composition caused by a given change in the value of the co-efficient $a$—and the smaller $\kappa$ is, the smaller is also the change in percentage composition.

Since the value of $P'_\beta - P_\beta$ will vary with the circumstances of each experiment, we cannot see from the general formula how near $\kappa$ must be to unity, in order that the change consequent on a given change in $a$ shall exceed the limit of experimental error. But that this formula is quite inapplicable to the case of ammonia and hydrogen, is seen by the fact that, if we replace in the formula the value of $a$ (for ammonia) as found by Carius by the correct value as since determined—thus causing a change of 15 per cent. in the value of $a$—we shall find that this change scarcely affects the calculated composition of the original gas, thus* —

---

* Carius, Ann. Ch. Pharm. xcix., p. 157.

| | | | Diff. |
|---|---|---|---|
| Eudiometric analysis, | per centage vol. of hydrogen | 3·74 | |
| Absorptiometric analysis ($a = 881{\cdot}85$) ........ | ” ” | 3·95 | 0·21 |
| Absorptiometric analysis ($a = 1018{\cdot}10$) ...... | ” ” | 4·04 | 0·09 |

$\beta = 0{\cdot}0193$.

The following numbers will still further justify this conclusion. The experiment is calculated for an increase in $a$ of 10 per cent. :—

*Ammonia and Hydrogen.**

| | | |
|---|---|---|
| Eudiometric analysis. | Hydrogen per cent. | 1·23 |
| Absorptiometric analysis $a = 864{\cdot}71$ ........ | ” ” | 0·97 |
| Absorptiometric analysis $a = 951{\cdot}12$ ........ | ” ” | 1·05 |

$\beta = 0{\cdot}0193$.

We may even *double* the co-efficient without causing any very great change :—

Thus calculating the experiment above with $a = 1729{\cdot}42$, we find

Hydrogen............ 1·41 per cent.

## II.—*Sulphurous Acid and Carbonic Acid in Water.*

The same method was employed to determine the solubility of this gas as for ammonia, with the necessary modifications in the analysis of the gas and of the solution.

The sulphurous acid was prepared from copper and sulphuric acid, and was washed through water and sulphuric acid; the carbonic acid was prepared from marble and hydrochloric acid, and was washed through water and dried by sulphuric acid and chloride of calcium. The gas was collected for analysis in tubes of about 100 cb. c. capacity, drawn out at each end and furnished with seven clamps to press the caoutchouc-joining, and thus to close the tube.

The volumes of these tubes were accurately determined, and the gas was allowed to pass through one of them, immersed in a bath of known temperature (about 30° C.), before it passed into the absorption bulb. After passing the gas through for about two hours, the bulb was sealed; the collecting-tube closed by pressing the caoutchouc-joinings connecting it with the rest of the apparatus by the screw-clamps; and the temperature of the bath and height of the barometer noted. The gas-tube was then opened under recently boiled water, and the sulphurous acid in solution determined with iodine-solution. The bulb and the ends having been weighed, it was broken under recently-boiled water, and the solution analysed volumetrically with standard iodine-solution.

---

* Carius, Ann. Ch. Pharm. xcix., 158.

The results of the experiments at 20° C. are given in Table E, where, as before, column I contains the percentage of sulphurous acid in the gas; II, the atmospheric pressure; III, the partial pressure on the sulphurous acid; IV, the weight absorbed by 1 grm. water; and V, the weight of sulphurous acid absorbed by 1 grm. water under the same direct pressure, as determined by Mr. Sims.

Table E.

| I. | II. | III. | IV. | V. |
|---|---|---|---|---|
| 6·16 | 753·1 | 45 | 0·008 | 0·008 |
| 16·71 | 768·3 | 124 | 0·017 | 0·020 |
| 17·99 | 768·8 | 135 | 0·021 | 0·021 |
| 28·10 | 756·0 | 208 | 0·032 | 0·031 |
| 29·80 | 756·5 | 216 | 0·032 | 0·032 |
| 31·60 | 750·8 | 232 | 0·032 | 0·035 |
| 51·10 | 762·6 | 381 | 0·055 | 0·056 |
| 54·70 | 762·4 | 407 | 0·058 | 0·058 |

Fig. 1 (p. 94) gives graphical representations of these results.

It will thus be seen that sulphurous acid, in mixture with carbonic acid, also obeys the same complicated law as under directly varied pressures, and therefore does not accord with the simple law of Dalton and Henry.

Table F.

| I. | II. | III. | I. | II. | III. |
|---|---|---|---|---|---|
| m. | gr. | | | | |
| 0·020 | 0·004 | 1·40 | 0·300 | 0·044 | 15·38 |
| 0·040 | 0·007 | 2·45 | 0·350 | 0·050 | 17·48 |
| 0·060 | 0·011 | 3·84 | 0·400 | 0·056 | 19·58 |
| 0·080 | 0·013 | 4·54 | 0·450 | 0·063 | 22·02 |
| 0·100 | 0·016 | 5·59 | 0·500 | 0·070 | 24·47 |
| 0·125 | 0·019 | 6·64 | 0·550 | 0·077 | 26·92 |
| 0·150 | 0·023 | 8·04 | 0·600 | 0·084 | 29·36 |
| 0·175 | 0·026 | 9·09 | 0·650 | 0·090 | 31·46 |
| 0·200 | 0·030 | 10·49 | 0·700 | 0·096 | 33·56 |
| 0·250 | 0·037 | 12·93 | 0·760 | 0·104 | 36·36 |

In Table F are contained the co-efficients of absorption for sulphurous acid under pressures less than 760. As before, column I contains the pressure; II, the weight of sulphurous acid absorbed by 1 gr. water; and III, the volume in cubic centimetres absorbed by 1 cb. c. of water.

The absorptiometric method is also inapplicable to the case of carbonic acid and sulphurous acid.

Schönfeld,[*] from experiments made in this way, came to the conclusion that sulphurous acid obeys the law of absorption. The numbers given below will conclusively prove that this result was fallacious, inasmuch as it is seen that an increase of 10 per cent. in the value of *a* causes no perceptible change in the calculated composition of the gas.

*Sulphurous Acid and Carbonic Acid.*[†]

| | | | | Diff. |
|---|---|---|---|---|
| Eudiometric analysis. | Sulphurous acid | per cent. | 35·812 | |
| Absorptiometric analysis $a = 67{\cdot}954$ ........ | ,, | ,, | 36·425 | 0·613 |
| Absorptiometric analysis $a = 74{\cdot}749$ ........ | ,, | ,, | 36·000 | 0·425 |

$\beta = 1{\cdot}4623$.

*Sulphurous Acid and Carbonic Acid.*[‡]

| | | | | Diff. |
|---|---|---|---|---|
| Eudiometric analysis. | Sulphurous acid | per cent. | 35·812 | |
| Absorptiometric analysis $a = 66{\cdot}114$ ........ | ,, | ,, | 36·115 | 0·303 |
| Absorptiometric analysis $a = 72{\cdot}725$ ........ | ,, | ,, | 35·985 | 0·130 |

## XI.—*On Mordenite, a New Mineral from the Trap of Nova Scotia.*

By Prof. How, D.C.L., University of King's College, Windsor, N.S.

The first known investigators of the mineralogy of Nova Scotia, Jackson and Alger, and Gesner, passing under the trap cliffs of the bay of Fundy, obtained such rich harvests of fine specimens of zeolitic and quartz minerals, that many a follower has trodden in their footsteps in hopes of like success. Whatever the relative good fortune in these cases, there is no doubt that year after year large quantities of beautiful objects have long been and are still carried away, to the enrichment of cabinets in different parts of the world. Beauty has been, no doubt, the desirable thing on most occasions, so that the chief attention of collectors has been given to such minerals (besides the quartz species) as stilbite, heulandite, analcime, apophyllite, and chabazite (especially in its often exquisitely red and pink-tinted variety, acadiolite, peculiar to this region), all of which certainly offer great attractions. Not only are these species attractive, but they present very decided differences in physical characters, so that they can be readily distinguished; whence it results that they have been long known and well described, as compared with another section of the zeolites, the fibrous species, which exhibit far less alluring forms, and resemble each other rather too closely for the unpractised eye to discern the differences which actually exist among them.

---

[*] Ann. Ch. Pharm. xcv., 12.

[†] Ibid, p. 17.

[‡] Ibid, p. 17.

A few years ago these fibrous zeolites were all called here either Thomsonite or Needlestone. I showed* first (in 1858) that mesolite is an abundant mineral in Nova Scotia trap, and that it is often associated with faroëlite, another fibrous mineral. The former, I imagine, is what passed for thomsonite, which species has probably not yet been found here. I have never met with it, and Mr. Marsh, of Yale College, U.S., who has on several occasions collected largely in various localities, states† that he has never found it, and he "considers it doubtful if this species has yet been discovered in this region." The name needlestone I take to have been given to natrolite, which is the other form in which the old "mesotype" is here represented. As minerals of this district, which were probably confounded with mesolite and faroëlite and misnamed along with them, I may mention the radiated lamellar gyrolite of Anderson, which I detected‡ in apophyllite, and the centrallasite of like structure, which I described§ as a new species a few years ago.

The subject of my present paper affords further proof that the fibrous zeolites occurring in Nova Scotia are more numerous than they were thought to be, for I shall show that it is different from any species yet described. The mineral I first met with in 1858, some two or three miles east of Morden or French Cross, a small village in King's county, on the shore of the bay of Fundy. It has, I have little doubt, been often found and rejected as a worthless incumbrance to the collector, on account of its wanting these marked features of lustre and colour displayed in large, or at least well-defined crystals, which are so generally the exclusive objects of his search. It occurs in rather small masses, varying from the size of a pigeon's to that of a bantam's egg, in the form of somewhat cylindrical, reniform, or flattened geodes and solid concretions, rather smooth externally, sometimes coated with a thin, yellowish crust, blotched with a green mineral, probably a silicate of iron, and sometimes exposing its own white, yellowish, or pinkish-coloured surface; often a small portion of the latter only is visible. It is hard enough to resist the weather better than the trap in which it is imbedded, so that it sometimes protrudes on old faces of rock, and is easily detached from its matrix with the chisel. Its interior often presents scarcely any appearance of crystalline structure, on the hurried glance generally taken on first exposing a fracture in collecting, as regards mordenite itself; and when other minerals are associated with it, these are, from the compactness of the geodes, in small or indistinct crystals. Even in the most compact specimens, however, a fibrous structure is seen on close examination, while in some cases this is so distinct that the mineral has probably been considered a compact variety of "thomsonite." To my eye, tolerably accustomed to the various forms of fibrous minerals met with in Nova Scotia trap, on some of which I had been working when I began to study it, the mineral looked unfamiliar in its general assemblage of characters; and I found on analysis that it differed essentially from any described species in the relative proportions of its elements, which are those of zeolites. This conclusion was arrived at from the examination of various specimens, in some of which it occurred with other minerals. Its associations are interesting, and afford material evidence as to its distinct nature. It is met with alone in solid concretions, also overlying a mineral in small, pale green, hemispherical, transluscent masses, looking like prehnite, but not agreeing in chemical characters with that species, so far as I could make out on the small amount of substance at my disposal; it occurs also underlying barytes, forming with it a solid mass, the heavy-spar occupying the entire centre; it also underlies apophyllite, which, in small well-defined crystals, lines the centre of a nearly solid geode. These characters were observed in the specimens from Morden, which served for analysis. Last summer I met with what I have no doubt is the same species at Peter's Point, or Margaretville, about eight miles to the west of Morden, occurring in several cases *per se*, and with flesh-coloured gyrolite in two specimens, one of which has but few of the small spherical concretions (about one-eighth of an inch in diameter) made up of the pearly plates characteristic of the latter species, while the other is thickly covered with them. It was in this neighbourhood that I detected gyrolite as a Nova Scotian mineral, in association with apophyllite, as described in the paper previously referred to.

---

* Silliman's Journal [2], xxvi, 31.

† *Ibid.* Jan. 1868.

‡ Edin. New Phil. Journal, 1861.

§ *Ibid.* x, 84.

Mordenite is a fibrous mineral, occurring in small concretions or geodes, as above described, of white, yellowish, or pinkish colour, and highly silky lustre, weathering dull; it cleaves readily in directions parallel with the fibres, is translucent on the edges; its hardness is a little above 5; it is rather brittle; its specific gravity is 2·08; before the blowpipe it fuses in a good heat without any inturmescence to a glassy bead; does not gelatinize, but affords slimy silica with hydrochloric acid.

In the following analyses, the mineral, not being perfectly decomposed by acids, was ignited for water, and the residue fused with carbonated alkali for the general analysis; the alkalies were extracted by acid in separate portions when determined; water was expelled with difficulty; the results are on substance dried over sulphuric acid.

| | I. | II. | III. | | IV. |
|---|---|---|---|---|---|
| Potassa | 0·09 | 0·23 | | | |
| Soda | 2·25 | 2·34 | 2·53[b] | 2·71[c] | 1·92[c] |
| Lime | 3·94 | 3·21 | 3·15 | 3·40 | 3·61 |
| Alumina[a] | 13·28 | 12·55 | 13·07 | 12·47 | 12·47 |
| Silica | 67·33 | 68·85 | 68·63 | 67·92 | 69·27 |
| Water | 12·88 | 13·32 | 12·70 | 13·50 | 12·73 |
| | 99·77 | 100·50 | 100·08 | 100·00 | 100·00 |

[a] With a very little $Fe_2O_3$. [b] KO not separated. [c] By loss.

Analysis I was on the mineral occurring alone; II, on the mineral with that resembling prehnite; III, on the mineral underlying apophyllite; in the second experiment the silica was proved to leave but a minute residue when boiled with carbonate of soda, consisting possibly of lime from the filter; IV was on the mineral with barytes; in this case the silica obtained, on being re-fused with carbonate of soda, gave a mass soluble in water, showing the mineral analysed to be free from heavy-spar.

The analytical numbers are sufficiently concordant to show constant composition in the different specimens, and the mean of them, with the oxygen of the constituents, is this,

| | Mean. | | Oxygen. |
|---|---|---|---|
| Soda ........ | 2·35 | = | ·606 |
| Lime ........ | 3·46 | = | ·988 |
| Alumina...... | 12·77 | = | 5·977 |
| Silica ........ | 68·40 | = | 36·238 |
| Water........ | 13·02 | = | 11·572 |
| | 100·00 | | |

The oxygen ratio for $RO.R_2O_3.SiO_3.HO$ is nearly 2 : 6 : 36 : 12, and taking (the half of) this as existing in the pure mineral, we arrive at the following simple formula expressive of the compositions of mordenite:—

$$RO.3SiO_3 + R_2O_3.3SiO_3 + 6HO;$$

and if $RO = \frac{1}{3} NaO + \frac{2}{3} CaO$, we get the following percentages:—

| | | | |
|---|---|---|---|
| $\frac{1}{3}NaO$ | = | 10·33........ | 2·54 |
| $\frac{2}{3}CaO$ | = | 18·66........ | 4·59 |
| $Al_2O_3$ | = | 51·40........ | 12·66 |
| $6SiO_3$ | = | 271·80........ | 66·92 |
| $6HO$ | = | 54·00........ | 13·29 |
| | | 406·19 | 100·00 |

showing a good general agreement with the results of the various analyses of the mineral occurring alone and in three distinct associations. It follows then that mordenite has the characters of a definite species; and, on comparing it with minerals containing the same elements, it is found to be nearest to heulandite in chemical composition. The formula of this mineral* is $CaO.SiO_3 + Al_2O_3.3SiO_3 + 5HO$, requiring 9·2 per cent. lime, 16·8 alumina, 59·3 silica, and 14·7 water, the silica being higher than in any other zeolite; but it is much lower than in the subject of this paper, so that mordenite stands out as the most highly silicated of the aluminous non-magnesian hydrous silicates yet described.

* Damour, *Dana's Mineralogy* ii, 330.

# XII.—*On a new Class of Organic Sulphur-compounds.*

By ADOLPH VON OEFELE.

Preliminary Notice.

(Communicated by Professor Kolbe.)

MONOSULPHIDE of ethyl, $(C_4H_5)_2S_2$ bids fair to be the source of a considerable number of new and interesting compounds. Of one of these, named diethylsulphone, I have already given a short description in "Liebig's Annalen" for September, 1863. This beautifully crystallised and very stable compound, which is easily obtained by treating monosulphide of ethyl with red fuming nitric acid, has the composition $(C_4H_5)_2[S_2O_4]$, analogous to that of the so-called sulphobenzide, $(C_{12}H_5)_2[S_2O_4]$. It may be compared with the ketone of propionic acid, $(C_4H_5)_2[C_2O_2]$, and is related to ethyl-sulphuric acid, $HO.(C_4H_5)[S_2O_4]O$, which is produced by the action of nitric acid on bisulphide of ethyl $(C_4H_5)S_2$, in the same manner as propione to propionic acid; thus—

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\}[C_2O_2] \qquad\qquad HO.(C_4H_5)[C_2O_2]O$$

Propione. Propionic acid.

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\}[S_2O_4] \qquad\qquad HO.(C_4H_5)[S_2O_4]O$$

Diethylsulphone. Ethylsulphuric acid.

In pursuing my experiments, I have further discovered that monosulphide of ethyl unites directly with iodide of ethyl, forming a beautifully crystallised compound, which dissolves easily in water and in alcohol, and crystallises again from these solutions, on evaporation, without volatilising with the water or alcohol vapour.

This compound is a true salt, viz., the iodide of the radicle, $(C_4H_5)_3S_2$, and has the composition $(C_4H_5)_3[S_2^{''''}].I$.

On mixing the aqueous solution of this salt with nitrate of silver, iodide of silver is precipitated, and nitrate of triethylsulphyl remains in solution. The iodide of triethylsulphyl is converted, by digestion with oxide of silver and water, into the hydrated oxide of triethylsulphyl, $(C_4H_5)_3[S_2^{''''}]O.HO$. which, by evaporating the solution, finally in the exsiccator, may be obtained in transparent deliquescent crystals.

Hydrated oxide of triethylsulphyl is a non-volatile, very powerful base, the aqueous solution of which has a strong alkaline reaction; it precipitates hydrated metallic oxides from their saline solutions, like caustic potash, and unites with acids, forming neutral salts. The *sulphate* and *hydrochlorate* are crystalline, but very deliquescent. The *chloroplatinate* $(C_4H_5)_3[S''''_2]\ Cl.PtCl_2$, crystallises readily from its aqueous solution on evaporation, in long prisms, apparently belonging to the quadratic system.

I am at present engaged on experiments which seem to show that this base, which contains *tetratomic* sulphur as its fundamental radicle, may be converted, by oxidation with nitric acid, into a compound of *hexatomic* sulphur, viz., $(C_4H_5)_3.[S_2O_2]O.HO$, which would perhaps still exhibit slight basic properties.

## XIII.—*On Acetanilide.*

### By C. GREVILLE WILLIAMS, F.R.S.

ACETANILIDE is one of the numerous substances formed by Gerhardt in 1852, by acting with the anhydrides of the monobasic acids, or the chlorides of their radicles, upon certain primary monamines. The reactions by which it is produced are sufficiently simple:

$$\begin{array}{ccccccc} Ꞓ_2H_3ƟCl & + & Ꞓ_6H_7N & = & Ꞓ_8H_9NƟ & + & HCl. \\ \text{Chloride of acetyl.} & & \text{Aniline.} & & \text{Acetanilide.} & & \end{array}$$

Or,

$$\begin{array}{ccccccc} Ꞓ_4H_6Ɵ_3 & + & 2(Ꞓ_6H_7N) & = & 2(Ꞓ_8H_9NƟ) & + & H_2Ɵ. \\ \text{Acetic Anhydride.} & & \text{Aniline.} & & \text{Acetanilide.} & & \end{array}$$

The above reactions are the only ones given in the Handbooks, but it is evident that to enable the decompositions of acetanilide to be studied minutely, some simpler process must be resorted to.

I found, in the beginning of last year, that the substance in question may be prepared in any quantity, and with extreme readiness, by cohobating aniline with strong acetic acid. The decomposition, of course, consists merely in the expulsion of water from the salt in accordance with the annexed equation:—

$$\begin{array}{ccccc} Ꞓ_8H_{11}NƟ_2 & = & Ꞓ_8H_9NƟ & + & H_2Ɵ. \\ \text{Acetate of aniline.} & & \text{Acetanilide.} & & \end{array}$$

But why acetate of aniline should so readily become dehydrated in the presence of water is not very clear.

On boiling the product of the reaction with water, and filtering the solution while hot, the compound is deposited on cooling in small crystals of perfect purity.

Another method consists in boiling the materials together for some time, and distilling until the product begins to solidify in the neck of the retort. The receiver being then changed, the acetanilide will distil over perfectly colourless. The neck of the retort must be kept very hot, to prevent the product from solidifying, and stopping it up. The first preparation I made in this manner gave the annexed numbers on combustion with chromate of lead.

0·2483 gramme gave 0·6506 carbonic acid and 0·1552 water. The formula, $\not{C}_8H_9N\not{O}$, requires the following numbers :—

| Experiment. | | Calculation. | | |
|---|---|---|---|---|
| Carbon........ | 71·46 | 71·11 | $\not{C}_8$ | 96 |
| Hydrogen .... | 6·94 | 6·67 | $H_9$ | 9 |
| Nitrogen...... | —— | 10·37 | N | 14 |
| Oxygen ...... | —— | 11·85 | $\not{O}$ | 16 |
| | | 100·00 | | 135 |

On boiling equal equivalents of ordinary glacial acetic acid and aniline together for one hour, and subsequently distilling, a quantity of the pure product will be obtained about equal in weight to the acid used.

I have lately been informed by Mr. Perkin, that acetanilide sometimes accompanies the crude aniline prepared on the large scale by Béchamp's process, especially if the acid used be very strong and in large excess.

Acetanilide presents itself, either as a white paraffin-like solid, or in small colourless plates, according as it has been obtained by distillation, or by crystallisation from water. It has a faint and characteristic odour. It melts at 100° C. according to Gerhardt, or at 101° according to my observations. The specific gravity of the fused product I found to be 1·099 at 10°·5.

It distils, as Gerhardt has stated, without decomposition. I find the boiling point to be 295° C., the atmospheric pressure at the time being 755 millimetres.

[illegible] ons of its vapour-density upon a very pure product. Owing to its extremely high boiling [illegible] n in an atmosphere of [illegible] by M. [illegible] Sainte Claire-Deville.

| | I. | II. |
|---|---|---|
| [illegible] | [illegible] grm. | 0 1412 grm. |
| Temperature of vapour | 350° | 350° |
| Temperature of air | 16° | 16° |
| Pressure | 755 millimetres | 766 mm. |
| Capacity of balloon | 92 cc. | 92·5 cc. |
| Residual air | 0·5 cc. | 0·25 cc. |
| Density | 4·887 | 4·807 |

| Mean. | Calculation* (2 vols) |
|---|---|
| 4·847 | 4,671 |

Although acetanilide bears the temperature of the boiling point of mercury as well as almost any organic substance, it nevertheless leaves a brownish residue in the balloon. This residue does not dissolve when the acetanilide is removed by means of alcohol. It is also insoluble in benzol, but may readily be removed by strong sulphuric acid.

Acetanilide dissolves readily in alcohol, ether, benzol, and essential oils. From a hot solution in lemon-oil it crystallises on cooling in large and beautiful needles. The alcoholic solution is not precipitated by water.

It dissolves very readily in warm sulphuric and hydrochloric acids. In nitric acid, kept cold, it also dissolves, with formation of nitraniline.† The nitro-compound is precipitated on addition of water.

Decomposed at a high temperature by means of sodium, acetanilide yields a considerable quantity of aniline, and a minute portion of basic oil of high boiling point, not yet fully examined.

From the facility with which acetanilide may now be prepared in any quantity, and at little cost, it will doubtless become the starting point of numerous researches.

---

* $H_2\Theta = 2$ vols.

† This reaction has been employed in researches by Dr. Hofmann and Mr. Mills.

## XIV.—*Conversion of Monocarbon-acids into the corresponding more highly Carbonated Dicarbon-acids.*

### By HERMANN KOLBE.

MONOCHLORACETIC acid heated with a moderately concentrated aqueous solution of cyanide of potassium, is easily decomposed, yielding chloride of potassium and cyanacetic acid. On subsequently boiling and evaporating the solution with excess of potash, a large quantity of ammonia is evolved; and if the alkaline mass be then supersaturated with dilute acetic acid, the resulting acid liquid shaken up with a large quantity of ether, and the clearly decanted ethereal solution evaporated, malonic acid, having a faint yellow colour, remains behind, and crystallises from aqueous solution, after treatment with animal charcoal, in large, very beautiful, limpid, four-sided tables.

Malonic acid thus obtained is identical with that prepared by Dessaignes from malic acid. Its formation from cyanacetic acid is easily explained by the following equation:

$$\underbrace{KO,C_2\left\{\begin{matrix}H_2\\C_2N\end{matrix}\right\}[C_2O_2]O}_{\text{Cyanacetic acid.}} + KO\,.\,3HO = \underbrace{2KO\,.\,(C_2H_2)''\begin{bmatrix}C_2O_2\\C_2O_2\end{bmatrix}O_2}_{\text{Malonate of potash.}} + H_3N.$$

I am at present engaged with the problem of converting, in like manner, propionic into succinic acid, and obtaining from mono- or di-carbon acids, also the tribasic tricarbon-acids.

The intermediate organic acids will form the subject of a special investigation.

---

## XV.—*On a New Formation of Malonic and Succinic Acids.*

### By HUGO MÜLLER.

WE are already acquainted with several reactions of chloracetic acid, which give a particular interest to this body. The facility with which the chlorine in this substance can be replaced by other elements, indicates, to a certain degree, a resemblance to the chlorides of the radicles; and, starting from this point of view, I considered it of great interest to ascertain whether the chlorine in chloracetic acid could also be replaced by cyanogen. If this should be the case, a body would result, belonging on the one hand, as cyanacetic acid, to the type of acetic acid, and capable, on the other hand, of deporting itself, under the influence of $2(H_2O)$, like the so-called nitriles, furnishing in this way an acid of the formula $C_3H_4O_4$, a term of the oxalic acid series.

My experiments have shown this supposition to be correct, and although they are not yet concluded, I am induced to lay before the Society the results hitherto obtained. A first experiment with the view indicated was made, by treating chloracetate of potassium with cyanide of potassium. A reaction took place in accordance with my expectation, but the result was not altogether satisfactory, on account of the final product containing an admixture of several other substances, the simultaneous formation of acetic and glycollic acids having been observed. This induced me to vary somewhat the mode of proceeding The employment of cyanide of silver appearing to promise a neat reaction, I considered it preferable to convert the chloracetic acid into chloracetic ether. The chloracetic ether does not, however, act with great energy on cyanide of silver (still less on cyanide of mercury), and in order to oppose to the silver a still greater affinity, I converted the chloracetic ether into iodacetic ether.

This was effected with great ease by following the plan employed by Perkin and Duppa for the conversion of bromacetic ether into iodacetic ether, viz., by simply heating an alcoholic solution of the ether with iodide of potassium. The iodacetic ether obtained in this way acts with facility upon cyanide of silver, and furnishes the cyanacetic ether.

Subsequently I found that the chloracetic ether acts also with the greatest facility upon pure cyanide of potassium, and, indeed, this method is by far the readiest for preparing cyanacetic ether.

For this purpose, the chloracetic ether is dissolved in alcohol, and to this solution is added a little more than the equivalent quantity of crystallised cyanide of potassium. A gentle heat causes a very perceptible reaction, and chloride of potassium is formed with rapidity; after finally boiling, the brownish-red, sometimes crimson-coloured solution is filtered off from the chloride of potassium, and the alcohol being distilled off, the cyanacetic ether remains in the retort.

The cyanacetic ether is obtained by distillation—which, on account of its high boiling point (above 200°), is best carried on in an atmosphere of hydrogen—in the state of a heavy oily liquid, of scarcely perceptible odour and sweetish taste.

On boiling this ether with a solution of potash, ammonia is evolved, and the decomposition being terminated, the solution furnishes with sulphate of copper a green precipitate, which by decomposition with sulphuretted hydrogen and evaporation of the aqueous solution, yields a beautifully crystallised acid, possessing all the properties of Dessaigne's malonic acid.

The special investigation of this interesting acid has prevented me hitherto from isolating the intermediate product, the cyanacetic acid. I hope, however, to be able to furnish an account of it hereafter.

Having by this reaction established the possibility of the transformation of the members of the acetic acid series into those of the oxalic acid series, I was induced to examine the deportment of chloropropionic acid in the same direction. I chose for this purpose, chloropropionic acid obtained from chloride of lactyl, according to Ulrich's method, and I succeeded in obtaining a small quantity of a crystalline acid, which on being heated, emitted the suffocating vapour so characteristic of succinic acid.

I take this for the present as a conclusive proof of the formation of succinic acid. Whether, however, this acid is the true succinic, and whether the acid derived from cyanacetic acid is identical with Dessaignes malonic acid, must be decided by a more complete investigation.

On comparing this new mode of formation of succinic acid with that from cyanide of ethylene, expressed in the following empirical formulæ:—

$$\underset{\text{Cyanopropionic acid.}}{C_3H_5(CN)O_2} + 2(H_2O) = \underset{\text{Succinic acid.}}{C_3H_5(CHO_2)O_2} + NH_3$$

$$\underset{\text{Cyanide of ethylene.}}{C_2H_4(CN)_2} + 4H_2O = \underset{\text{Succinic acid.}}{C_2H_4(CHO_2)_2} + 2(NH_3),$$

the analogy becomes apparent, and according to this, the formation of cyanopropionic acid, as the first phase of the transformation of the cyanide of ethylene, obtains some probability.

The introduction of cyanogen into certain molecules, and the subsequent action of $2(H_2O)$ thereon, causes an addition of $CO_2$, which renders possible the synthetic formation of bodies of homologous series, the terms of which differ from each other by the increment, $CO_2$. For instance, starting with the hydride of ethyl $C_2H_6$, the following series may be obtained by this reaction :—

$$\underset{\text{Cyanide of ethyl.}}{C_2H_5(CN)} + 2H_2O = \underset{\text{Propionic acid.}}{C_3H_6O_2} + NH_3$$

$$\underset{\text{Cyanopropionic acid.}}{C_3H_5(CN)O_2} + 2H_2O = \underset{\text{Succinic acid.}}{C_4H_6O_4} + NH_3$$

$$\underset{\text{Cyanosuccinic acid.}}{C_4H_5(CN)O_4} + 2H_2O = \underset{\text{New acid.}}{C_5H_6O_6} + NH_3, \&c.$$

The last two terms are still wanting.

---

## XVI.—*On Thallium.*

### By William Crookes, F.R.S.

In the present paper it is intended to collect together the various chemical and physical facts relating to thallium, accumulated during the few years which have elapsed since its discovery. The main body of the paper will be condensed from my own researches, already published in the *Philosophical Transactions*, the *Chemical News*, and elsewhere; it will also contain the results of many experiments which are now published for the first time; but I shall also freely make use of the researches of other chemists, where necessary, to fill up any gaps in the history of this metal. I shall follow the arrangement adopted in Gmelin's Handbook, and in cases where no authority is given for a statement, it may be accepted as resting upon my own experiments.

#### LIST OF MEMOIRS RELATING TO THALLIUM.

W. Crookes, *On the Existence of a New Element, probably of the Sulphur Group.*—Chemical News, iii, 193 (March 30, 1861), and Phil Mag. [4] xxi, 301. ——*Further Remarks on the supposed New Metalloid.*—Chemical News, iii, 313 (May 18, 1861).——*Thallium, a New Metallic Element.*—International Exhibition, May 1, 1862.

A. Lamy, *Verbal Communication on a Yellow Crystalline Substance.*—Société impériale des Sciences de Lille. May 2, 1862.——*Verbal Communication on a Metal supposed to be Thallium, obtained from the yellow crystalline substance.* Société impériale des Sciences de Lille. May 16, 1862.

W. Crookes, *Preliminary Researches on Thallium.*—Proceedings of the Royal Society, xii, 150 (June 19, 1862), and Chemical News, v, 349 (July 5, 1862).

A. Lamy, *On the Existence of a New Metal, Thallium.*—Comptes rendus, liv, 1255 (June 23, 1862).

F. Kuhlmann, *On some Compounds of Thallium with Organic Acids.*—Comptes rendus, lv, 607; Ann. Ch. Pharm. cxxvi, 75.

De la Provostaye, *On the Crystalline Form of some Salts of Thallium.*—Comptes rendus, lv, 610; Ann. Ch. Pharm. cxxvi, 79.

W. Crookes, *On the Discovery of Thallium.*—Cosmos, xxi, 628 (December 5, 1862).

A. Lamy, *Further Observations on Thallium.*—Comptes rendus, lv, 836 (December 8, 1862).—— *On the Discovery of Thallium.*—Cosmos, xxi, 680 (December 19, 1862).

Dumas, *Report on a Memoir of M. Lamy, relative to Thallium.*—Comptes rendus, lv, 866; Chemical News, Jan. 10, 1863; Ann. Ch. Phys. [3], lxvii, 418.

Regnault, *On the Specific Heat of Thallium.*—Comptes rendus, lv, 887; Ann. Ch. Pharm. cxxvi, 82.

W. Crookes, *The Discovery of the Metal Thallium.*—Chemical News, Jan. 10, 1863.

Werther, *Presence of Thallium in Commercial Tellurium.*—J. pr. Chem. lxxxviii, 180.——*Presence of Thallium in a deposit from a sulphuric acid manufactory.*—J. pr. Chem. lxxxviii, 192.

W. A. Miller, *Note on the Spectrum of Thallium.*—Proceedings of the Royal Society, xii, 407, and Chemical News, March 28, 1863.

M. Mascart, *Note on the Spectrum of Thallium.*—Comptes rendus, lvi, 139.

F. Kuhlmann, *On the Deposit in the Leaden Chambers of Sulphuric Acid Works.*—Comptes rendus, lvi, 171 (Jan. 26, 1863).

W. Crookes, *On Thallium.*—Philosophical Transactions, Feb. 5, 1863.

W. B. Herapath, *On Thallium in Medicinal Preparations of Bismuth.*—Chemical News, Feb. 14, 1863.

W. Crookes, *Analytical Notes on Thallium—Separation of Thallium from Bismuth.*—Chemical News, March 7, 1863.

A. Matthiessen & C. Vogt, *On the Influence of Temperature on the Electric Conducting power of Thallium and Iron.*—Philosophical Transactions, March 12, 1863.

W. Crookes, *Analytical Notes on Thallium—Separation of Thallium from Copper.*—Chemical News, March 21, 1863.——*Separation of Thallium from Cadmium.*—Chemical News, March 28, 1863.

L. De La Rive, *On the Conducting Power of Thallium for Electricity.*—Comptes rendus, lvi, 588 (March 31, 1863).

W. Crookes, *On the Discovery of the Metal Thallium.*—Proceedings of the Royal Institution, March 27, 1863; and Chemical News, April 11, 1863.

A. Lamy, *On the Existence of a New Metal, Thallium.*—Ann. Ch. Phys., April, 1863.

Viktor von Lang, *On the Crystalline Form and Optical Properties of Sulphate of Thallium.*—Phil. Mag. [4] xxv, 248.

W. Crookes, *Analytical Notes on Thallium—On the Presence of Thallium in Commercial Hydrochloric Acid—Separation of Thallium from Iron.*—Chemical News, April 25, 1863.

W. T. Roepper, *On Thallium in Furnace products.*—Silliman's Journal, [2], xxxv, 420 (May, 1863).

W. Crookes, *Analytical Notes on Thallium—Separation of Thallium from Copper.*—Chemical News, May 9, 1863.

R. Böttger, *On the Extraction of Thallium from the Lead Chamber Deposit at the Sulphuric Acid Manufactory of Oker, and on some Compounds of this Metal.* —J. pr. Chem. xc. 22; Ann. Ch. Phys. cxxvi, 175.——*On the Extraction of Thallium from the Flue Dust of a Sulphuric Acid Manufactory.*—J. pr. Chem. xc. 30; Ann. Ch. Pharm. cxxvi, 266.

W. Crookes, *Contributions to the History of Thallium—Peroxide of Thallium.* Chemical News, June 20, 1863.

J. Müller, *Determination of the Length of the Wave of the Green Thallium Line.*—Pogg. Ann. cxviii, 641; Phil Mag. [4], xxvi, 259.

W. Crookes and A. H. Church, *Contributions to the History of Thallium.* —Chemical News, July 4, 1863.

W. Crookes, *On the Discovery of the Metal, Thallium.*—Phil. Mag. [4], xxvi, 55.

Erdmann and Werther, *On the Thalliferous Deposits of Leaden Chambers.* J. pr. Chem. lxxxviii, 377.

E. Willm, *On the Estimation of Thallium by means of Permanganate of Potash.* —Bulletin de la Société Chimique de Paris, 1863, p. 352; Chemical News, August 29, 1863.

E. Willm, *On the Ammoniacal Compounds of Perchloride of Thallium.*—Bulletin de la Société Chimique de Paris, 1863, p. 354.

W. Crookes, *On the Extraction of Thallium on a large scale from the Flue Dust of Pyrites Burners.*—British Association, September 1, 1863; Chemical News, October 3, 1863, Cosmos, October 30, 1863.

A. Lamy, *On the Poisonous Effects of Thallium.*—Comptes rendus, lvii, 442; Chemical News, September 12, 1863.

R Böttger, *On the Presence of Thallium in the Mineral Waters at Nauheim.* —Ann. Ch. Pharm. cxxvii, 368; J. pr. Chem. xc, 145.——*On a Simple Method of Extracting Thallium from Flue Dust.*—J. pr. Chem. xc. 151.

Erdmann, *On the Position of Thallium in the Classification of Metals.*—J. pr. Chem. lxxxix, 378.

J. Nicklès, *On the Position of Thallium in the Classification of Metals.*— J. Pharm. [3], xlvi, 362.

W. Crookes, *Contributions to the History of Thallium—Nitrate of Thallium. Perchlorate of Thallium,* Chemical News, October 24, 1863.——*Phosphate of Thallium,* Ibid, Nov. 7, 1863.——*Carbonate of Thallium.*—Ibid, November 14, 1863. ——*Sulphate of Thallium.*—Ibid, November 21, 1863.——*Chromate of Thallium.* —Ibid, November 28, 1863.

Schrötter, *On the Presence of Thallium in Lepidolite and Mica.*—Wien. Akad. Ber., December 3, 1863.

W. Crookes, *Contributions to the History of Thallium—Acetate of Thallium.* —Chemical News, December 12, 1863.—*Oxalate of Thallium.*—Chemical News, January 2, 1864.

J. Nicklès, *Notes on the Spectral Ray of Thallium.*—Comptes rendus, lviii, 132; Chemical News, January 30, 1864.

J. Nicklès, *On an Iron and Thallium Alum.*—J. de Pharm. xlv, 24, 140.

Bischoff, *On the Presence of Thallium in Binoxide of Manganese.*—Ann. Ch. Pharm. cxxix, 375.

W. Crookes, *On the Solubility of some Thallium-salts.*—Chemical News, Jan. 23, 1864.——*On the Spectrum of Thallium.*—Ibid, January 30, 1864.

*History.*—Thallium was discovered in March, 1861, in a seleniferous deposit from the sulphuric acid manufactory at Tilkerode, in the Harz Mountains. In the distillation of some impure selenium prepared from this deposit, a considerable residue was left behind in the retort. This was at first thought to contain tellurium, until spectrum analysis showed me that a new element was present, whose spectrum consisted of a single, sharp, and brilliant green line. The element was at first suspected to be a metalloid, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by myself in September, 1861, and was afterwards exhibited in the International Exhibition, May 1, 1862, labelled "Thallium, a New Metallic Element." On the 16th of the same month, M. Lamy exhibited at the Imperial Society of Lille, a piece of metallic thallium, which was also deposited in the International Exhibition in June.

The name *thallium* is derived from the Greek word *θαλλὸς*, a green bud.

*Sources.*—As sulphide, thallium is a very widely distributed constituent of iron and copper pyrites. Upon examining a large collection of pyrites from different parts of the world, it was found present in more than one-eighth. It is not confined to any particular locality. Amongst those ores in which it occurs most abundantly (although in these cases it does not constitute more than from the 100,000th to the 4,000th bulk of the ore), may be mentioned iron pyrites from Theux near Spa in Belgium, from Namur, Philipville, Alais, the South of Spain, France, Ireland, Cornwall, Cumberland, and different parts of North and South America; in copper pyrites from Spain, as well as in crude sulphur prepared from this ore; in blende and calamine from Theux; in blende, calamine, metallic zinc, sulphide of cadmium, metallic cadmium, and cake sulphur from Nouvelle-Montagne; in native sulphur from Lipari and Spain; in bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals (frequently in so-called pure medicinal preparations of these metals); in commercial selenium and tellurium (probably as selenide and telluride).

Thallium is likewise frequently present in copper and commercial salts of this metal. In Spain a very impure copper is prepared in the following way:—Copper pyrites is allowed to oxidise in the air, and the resulting sulphate of copper is washed out; scrap iron is now placed in the liquid, which causes the copper to precipitate in the powdery state. The metal is then collected together, dried, strongly compressed, and heated to the melting point. It is brought over to this country in the form of rectangular cakes, weighing about 20 lbs. each. The sulphide of thallium, oxidising to sulphate along with the sulphide of copper, is washed out by the water, and precipitated with the copper by the iron. The two metals readily alloy together.

Thallium is also present in tolerable quantity in lepidolite from Moravia, and in mica from Zinnwald (Schrötter). It has likewise been found in the deliquescent "Sel-à-Glace" from the mother-liquors of the salt-works at Nauheim. This consists of a mixture of the chlorides of magnesium, potassium, and sodium, with relatively considerable quantities of chlorides of rubidium and cæsium, and sensible traces of chloride of thallium (Böttger). This mineral water is said by Böttger, to be the richest natural source of thallium. The quantity present is not stated but it is not likely to be richer than the Theux pyrites, which contains 1 in 4000.

Many samples of commercial sulphuric acid and yellow hydrochloric acid contain thallium. The source in these cases is evidently the pyrites used in the sulphuric acid works.

The optical process of detecting thallium in a mineral is very simple. A few grains only of the ore have to be crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen's gas-burner, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opaque screen in the eye-piece of spectroscope to protect the eye from the glare of the sodium-line, I have, in half a grain of mineral, detected thallium when it was present only in the proportion of 1 to 500,000.

The sensitiveness of this spectrum reaction is so great that no estimate can be arrived at respecting the probable amount of thallium present. Before deciding whether a deposit or mineral contains sufficient of the metal to be worth extracting, it is necessary to make a rough analysis in the wet way by methods described in the next section.

*Preparation. a. From Iron pyrites.*—The pyrites from the Société Anonyme de Rocheux et d'Oneux, Theux, contains about 1 part of thallium in 4,000. Two tons of this ore, which I owe to the kindness of Professor Chandelon, were worked in the following manner:—

The pyrites, broken up into pieces of the size of a walnut, is distilled in hexagonal cast iron pipes, closed at one end, and arranged in a reverberatory furnace. Conical sheet-iron tubes are luted on to the open ends, and the retorts are kept at a bright red heat for about four hours. At the end of the operation, the receivers will be found to contain from 14 lbs. to 17 lbs. of dark green or grey-coloured sulphur for every 100 lbs. of ore used. The whole of the thallium originally in the pyrites will be found in this sulphur, from which it has now to be separated. The sulphur may be dissolved out by means of bisulphide of carbon, which leaves the sulphide of thallium behind; or it may be extracted by boiling with caustic soda. The former plan occasions less loss of thallium, but owing to the inconvenience of working with large bulks of bisulphide of carbon, I prefer the soda process. 12 lbs. of caustic soda, 18 lbs. of the thalliferous sulphur, and 1½ gallons of water are boiled together till the sulphur has dissolved; 6 gallons of water are added, and the clear liquid, when cool, is decanted from a voluminous black precipitate, which has been separated from the sulphur. The precipitate is then collected on a calico filter and washed. It contains the greater portion of the thallium in the form of sulphide, together with iron, copper, mercury, zinc, &c. Some thallium, however, remains dissolved in the alkaline liquid and is lost. The black precipitate is then dissolved in hot dilute sulphuric acid, to which a little nitric acid is added, and the liquid is diluted with water and filtered. Hydrochloric acid and sulphite of soda will now throw down the nearly insoluble, white, protochloride of thallium, which is to be filtered off and washed.

*b. From Sulphur or Pyrites in the wet way.* The material is dissolved in nitro-hydrochloric acid, until nothing but bright yellow sulphur is left; water is then added, and the filtrate is evaporated with sulphuric acid, until it is nearly dry, and sulphuric vapours are copiously evolved. The residue is dissolved in large excess of hot water, and carbonate of soda is added to alkaline reaction, and then cyanide of potassium (free from sulphide of potassium). The liquid is then heated gently for some time, and filtered. The precipitate contains the whole of the lead and bismuth which may be present, as carbonates, whilst the thallium is in solution. A current of sulphuretted hydrogen being now passed through the liquid, precipitates all the thallium, whilst the copper, antimony, tin, and arsenic remain dissolved. The precipitated sulphide is filtered off, washed, and dissolved in dilute sulphuric acid, and the thallium is precipitated as chloride, by means of hydrochloric acid.

*c. From the flue-dust of Pyrites-burners.* This is by far the most economical source of thallium at present known. In burning thalliferous pyrites for the purpose of manufacturing sulphuric acid,* the thallium oxidises along with the sulphur, and is driven off by the heat. If the passage leading from the burners to the leaden chambers is only a few feet long, the greater portion of the thallium escapes condensation, and volatilises into the leaden chambers; it there meets with aqueous vapour, sulphurous and sulphuric acids, and becomes converted into sulphate of the protoxide of thallium. This being readily soluble both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution and accompanies the sulphuric acid in its subsequent stages of concentration, &c. If, on the other hand, the passage connecting the burners and chambers is 10 or 15 (or more) feet in length, nearly the whole of the thallium is condensed, together with the multiplicity of other bodies which constitute "flue-dust." Accompanying the thallium, I have found mercury, copper, lead, tin, arsenic, antimony, iron, zinc, cadmium, bismuth, lime, and selenium, together with ammonia, sulphuric, nitric, and hydrochloric acids. The amount of thallium in these flue-deposits is very various. In many specimens it is not present at all, and in very few it amounts to as much as ¼ per cent., although in some I have found as much as 8 per cent. of thallium. The plan I prefer for extracting the metal from the dust is the following which has been practically tested in Messrs. Hopkin and Williams' laboratory, on nearly 10 tons of material. The dust is first mixed in wooden tubs with an equal weight of boiling water, and is well stirred; during this operation a considerable quantity of nitrous acid is evolved; after which the mixture is allowed to rest for 24 hours for the undissolved residue to deposit. The liquid is then syphoned off, and the residue is washed, and afterwards treated with a fresh quantity of boiling water. The collected liquors, which have been syphoned off from the deposit, are allowed to cool, precipitated by the addition of a considerable excess of strong hydrochloric acid, and the precipitate, consisting of very impure chloride of thallium, is allowed to subside. The chloride obtained in this way is then well washed on a calico filter, and afterwards squeezed dry. Three tons of the dust have yielded as much as 68 pounds of this rough chloride.

The next step consists in treating the crude chloride in a platinum dish with an equal weight of strong sulphuric acid, and afterwards heating the mixture to expel the whole of the hydrochloric acid. To make sure of this, the heat must be continued until the greater part of the excess of sulphuric acid is volatilised. After this the mass of bisulphate of thallium is dissolved in about 20 times its weight of water, and the solution filtered. On the addition of hydrochloric acid to this solution, nearly pure chloride of thallium is thrown down; this is collected on a calico filter, well washed, and then squeezed dry. Lamy recommends that the highly acid flue-dust be previously calcined to get rid of the hydrochloric acid. This is useful when working on the small scale and with a limited supply of material, but the saving of thallium is so trifling, that it is not worth the extra trouble when working on many cwt. of dust.

*d. From the Saline Residues of the Salt-works at Nauheim.* Böttger adds an insufficient quantity of bichloride of platinum to the strong solution, and boils the precipitate 5 or 6 times with three times its weight of water. The insoluble residue consists of the platinum-salts of cæsum, rubidium, and thallium. Upon boiling these with a weak solution of potash and a little hyposulphite of soda, the solution soon becomes clear, whereupon cyanide of potassium and sulphuretted hydrogen are added. This precipitates the thallium as sulphide. The liquid is then to be filtered, the residue washed and dissolved in sulphuric acid, and the metal precipitated by metallic zinc.

*e. From Commercial Hydrochloric Acid.* Many samples of yellow hydrochloric acid contain thallium. It may be separated by neutralising with an alkali and adding sulphide of ammonium. The black precipitate contains the thallium, together with iron and some other metallic impurities of the acid. It is to be dissolved in sulphuric acid, and the thallium precipitated with hydrochloric acid as protochloride.

*Purification.* The crude protochloride of thallium obtained by either of the above methods is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused bisulphate is now to be dissolved in an excess of water, and an abundant stream of sulphuretted hydrogen passed through the solution. The precipitate, which may contain tin, arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrosulphuric acid is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron and alumina, which generally appears in this place, is filtered off, and the clear solution evaporated to a small bulk. Sulphate of thallium will then separate out on cooling in the form of long, clear prismatic crystals. As sulphate of ammonia is much more soluble than sulphate of thallium, the latter can readily be separated from the small quantity of the former salt present. The two salts do not crystallise together.

In order to avoid the inconvenience of driving off the excess of oil of vitriol in the decomposition of chloride of thallium, it may in some cases be preferable to proceed as follows:—Boil the chloride of thallium in solution of sulphide of ammonium for five minutes: decomposition takes place readily. Filter and wash with hot sulphuretted water till no more chlorine can be detected in the filtrate, then dissolve the sulphide on the filter in dilute sulphuric acid, and treat the solution with ammonia, &c., as above directed.

In order to obtain the metal, sulphate of thallium is dissolved in twenty times its weight of water; the liquid is acidulated with sulphuric acid, and a current of electricity from two or three cells of Grove's batteries is passed through it, platinum terminals being used. The appearance presented when a tolerably strong solution of thallium is undergoing reduction is very beautiful. If the energy of the current bears a proper proportion to the strength and acidity of the liquid, no hydrogen is evolved at the negative electrode, but the metal grows from it in large crystalline fern-like branches, spreading out into brilliant metallic plates, and darting long needle-shaped crystals, sometimes upwards of an inch in length, towards the positive pole, the appearance strikingly resembling that known as the tin tree. Some of the tabular crystals, as seen in the liquid, are beautifully sharp and well defined, their angles appearing temptingly measurable; considerable difficulty is, however, met with in disengaging them from the electrode, and removing them in a perfect state from the liquid. So long as thallium is present in the solution, no hydrogen is evolved with a moderate current; as soon as bubbles of gas begin to form, the reduction may be considered complete. The crystalline metallic sponge may now be squeezed into a compact mass round the platinum terminal, disconnected from the battery, quickly removed from the acid liquid, rinsed with a jet from a wash bottle, and transferred to a basin of pure water. The metal is then carefully removed from the platinum, and kneaded with the fingers into as solid a lump as possible. It coheres together readily by pressure, and will be found to retain its metallic lustre perfectly under water.

When considerable quantities of thallium are to be reduced to the metallic state, it is convenient to employ metallic zinc for the purpose. In the course of twenty-four hours, upwards of a quarter of a hundred weight of metal was reduced in the following way :—Plates of pure zinc (which should leave no residue whatever when dissolved in sulphuric acid) are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallised sulphate of thallium, in quantities of about seven pounds at a time, is then placed in the dish, and water poured over to cover the salt. Heat is applied, and in the course of a few hours, the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zincs removed, and the spongy thallium washed several times. It is then strongly compressed between the fingers, and preserved under water until it is ready for fusion.

The metal is readily obtained in the coherent form by fusing the sponge. This is most conveniently performed under cyanide of potassium on the small scale, and under coal gas when working with large quantities. In the former case the sponge, strongly compressed and quite dry, is broken into small pieces, which are dropped one by one into cyanide of potassium kept fused in a porcelain crucible. They instantly melt, forming a brilliant metallic button at the bottom. When cold, the cyanide of potassium may be dissolved in water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified.

On the large scale, the fusion is best effected in an iron crucible. This is placed over a gas-burner, and a tube is arranged so that a constant stream of coal-gas may flow into the upper part of the crucible. Lumps of the compressed sponge are then introduced, one after the other as they melt, until the crucible is full of metal. It is then stirred up with an iron rod, and the thallium may either be poured into water and obtained in a granulated form, or cast into an ingot. Thirty or forty fusions have been performed in the same crucible without the iron being acted upon in the least by the melted thallium.

*Properties.* Thallium is a perfect metal with high metallic lustre. In colour it most resembles cadmium, not being so brilliantly white as silver, but free from the blue tinge of lead. The true colour can scarcely be seen by cutting or scraping the surface, as it tarnishes too quickly. It is best observed by scraping the metal under water, or by fusing it in hydrogen and allowing the melted globule to flow away from the dross. When fused under coal-gas, the liquid metal in the crucible can hardly be distinguished from mercury. It is susceptible of taking a very high polish by friction with appropriate materials, under water. Thallium tarnishes at ordinary temperatures, quickly becoming coated with a film, which almost entirely protects it from further action of the air. The specific gravity of thallium varies according to the treatment it has undergone. A lump melted and slowly cooled under cyanide of potassium was found to be as light as 11·81. After being strongly compressed it became 11·88. When *squeezed* into wire, a portion was found to be as high as 11·91. M. Lamy gives it as 11·86. M. De la Rive states it to be 11·85 after being melted, and 11·80 after being *drawn* into wire. It is the softest known metal admitting of free exposure to the atmosphere. The finger-nail, and even a piece of lead, scratch it readily. It marks paper like plumbago, forming a streak, grey at first, then turning yellow, and in a day or two fading nearly out. Sulphide of ammonium or sulphuretted hydrogen will at any time temporarily restore the dark streak. Thallium has less tenacity than lead, and does not become brittle at any temperature between 0°F. and its melting-point. It is very malleable, and can be hammered into foil as thin as tissue paper. When hammered it does not become sensibly harder. It can be drawn into wire only with difficulty, but it is squeezed into wire very readily by the process technically known as "squirting." Thallium wire is almost devoid of elasticity, retaining any form into which it is bent, with scarcely a tendency to spring to its original position. When first prepared the wire appears amorphous, and will remain so if kept at the ordinary temperature in carbonic acid or petroleum free from air. In water it gradually becomes crystalline, resembling the *moiré* of tin plate; this effect is immediately produced when thallium in wire, ingot, or plate, tarnished or clean, is boiled in water.

Thallium is a very crystalline metal, and crackles almost as much as tin when bent. When several pounds of the metal are fused and allowed to cool slowly, and the interior liquid portion poured off from that which has solidified, well-defined crystals in octahedrons and fern-like forms are produced. The melting-point of thallium is 561° F. (according to Lamy, 554° F.). In an experiment in which about two pounds of chemically pure metal were fused in an iron crucible, and the temperature taken by means of a thermometer specially made for this purpose by Mr. Casella, the mercury stood at 561° F. (293·9° C.) during the whole of the time the thallium was solidifying. The bulb of the thermometer was perfectly covered by the melted metal, and it was kept constantly moving. Thallium does not become pasty; it expands considerably before complete fusion, and contracts strongly on cooling. Two pieces of the metal weld together under strong pressure at the ordinary temperature, and after filling a steel die with scraps and cuttings, they may be readily squeezed into a solid rod apparently as tenacious as when obtained by fusion.

Thallium, when heated in the air, begins to volatilise at a red heat, evolving brown vapours of oxide; it boils below a white heat, and may be distilled in a current of hydrogen. The hydrogen takes up mechanically a little thallium, which is not deposited upon traversing five feet of cold glass tubing, as the emergent gas, when ignited, burns with a bright green flame.

When heated to redness and plunged into oxygen, thallium burns brilliantly (Lamy). Before the blowpipe, on charcoal, the metal melts instantly, and evolves copious brown fumes. If the bead is heated to redness, it glows for some time after the source of heat is removed, continually evolving vapours which appear to be a mixture of metal and oxide. On cooling, the adjacent parts of the charcoal are found to be coated with small globules of volatilised metal, surrounded with a reddish amorphous sublimate of mixed proto- and peroxide. The principal globule of metal will also be coated with a fused layer of protoxide, resembling lead in this respect. When thallium is heated in an open glass tube, it melts and becomes rapidly converted into the more fusible protoxide, which strongly attacks the glass. This oxide is of a dark-red colour when hot, solidifying to a brown crystalline mass.

Some of the compounds of thallium are very volatile, the chlorides, for instance, distilling with the vapour of water, and volatilising when heated to a temperature below redness. Other compounds, such as the sulphate and phosphate, will bear a full red heat without experiencing any loss. Thallium compounds are not, therefore, nearly so volatile as mercury-salts.

The most characteristic property of thallium is the intense green colour which the metal or any of its compounds communicates to a colourless flame. When examined in the spectroscope this colour is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line, coinciding with the number 1442·6 on the magnificent chart of the spectrum given by Kirchhoff, in the memoirs of the Berlin Academy for 1861. The thallium spectrum is simpler than that of any other element yet examined. An amplifying power as great as has ever been applied to the spectrum (16 heavy glass prisms), does not affect the integrity of the line, and the high temperature of the hydrogen or oxyhydrogen flame shows no new lines; thallium has therefore a simpler spectrum than sodium or lithium, which stand next to it in this respect.

The length of the wave of the green thallium line has been determined by Dr. J. Müller. He finds it to be 0·0005348 millimetre.

When sparks from an induction-coil are passed between two pieces of thallium wire, Dr. W. A. Miller finds that the light ceases to be purely monochromatic. When viewed by the spectroscope, several new lines make their appearance; besides the usual intense line in the green, five others are particularly observable: first, a very faint one in the orange; next, two of nearly equal intensity in the green, more refrangible than Tl $\alpha$, with a third, much fainter, these three lines in the green being nearly equidistant; whilst, fifth, in the blue is a bright, well defined line. Dr. Miller has also examined the photographic spectrum of thallium; it contains several very characteristic groups of lines, recalling the features of the spectra of cadmium and zinc, and less strongly that of lead. For a detailed description the reader is referred to Dr. Miller's paper, quoted at the commencement.

The thallium line has no counterpart in the black lines of the solar spectrum.

The delicacy of the spectral reaction of thallium is very great. Experiments tried with solutions of definite strength show that the 5-millionth of a grain of sulphate of thallium is sufficient to produce the spectrum reaction.

Nicklès states that certain sodium-compounds possess an antagonistic action to the green thallium line in the spectrum; that they possess a paralysing action on the thallium light, chloride of sodium especially having the property of obscuring the green ray. The experiments which he adduces in proof of this are by no means satisfactory, and several of his statements are decidedly erroneous. On the other hand, I have shown that when thallium is burnt in the presence of nearly a thousand times its weight of chloride of sodium, there is not the least interference between the two lines, which glow side by side, in total indifference as to each other's existence.

When a grain or two of metallic thallium is placed in a cup-shaped cavity in the lower carbon pole of an electric lamp, connected with 30 or 40 cells of a nitric acid battery, after making contact, the two poles can be separated for the space of an inch or more, voltaic connection being maintained by the bridge of thallium vapour rising from the cup. If projected on a screen, the arc is seen to emit absolutely homogeneous green light, and if passed through an appropriate arrangement of slit, prisms, and lenses, the green band of the spectrum will be projected of intense brilliancy, on a nearly black background.

Thallium is powerfully repelled by both poles of an electro-magnet, nearly equalling bismuth in diamagnetic character.

The electric conductivity has been examined by Dr. Matthiessen and M. De la Rive. Taking silver as 100, the former experimentalist finds it to have a conducting power of 9·16, whilst De la Rive gives it as 8·64; in either case, it lies between tin and lead. Drs. Matthiessen and Vogt find that the conducting power of thallium decreases between 0° and 100° C., 31·420 per cent., which is a larger per centage decrement than that obtained for many other pure metals, namely, 29·307 per cent. The specific heat of thallium is given by Lamy at 0·0325, and by Regnault, at 0·03349 and 0·03361.

The atomic weight of thallium has been found by Lamy to be 204. My own determinations give, as the mean results of five experiments, 202·96. This subject is now under accurate investigation; the experiments are not yet completed, but as far as I am able to judge, they point to an atomic weight somewhat lower than the number I have given.

Thallium is easily reduced to the metallic state. When in aqueous solution, the metal is readily obtained by an electric current, or by the reducing action of metallic zinc. In the dry state, its salts may be reduced by carbon and carbonate of soda at a high temperature, or from the chloride by an alkali-metal under the influence of heat. The pure metal is scarcely attacked by hydrochloric acid, even when boiling. It is dissolved somewhat more readily by sulphuric acid, especially if it be in contact with a piece of platinum; nitric acid attacks it violently.

In electro-chemical position, thallium is very near cadmium, being precipitated from the sulphate by zinc and iron, but not by cadmium, tin, or copper.

Several thallium-salts are sensitive to light; the protochloride darkens readily, although with by no means the rapidity of chloride of silver.

The position of thallium amongst elementary bodies has given rise to considerable discussion. On the continent it is generally classed amongst alkali-metals; in England it is, on the other hand, generally regarded as belonging to the silver and lead group. I give below the arguments which have been adduced on both sides.

In favour of the relationship of thallium to the alkali-metals, the following facts have been adduced:—It forms a readily soluble, highly alkaline oxide, a soluble and alkaline carbonate, an insoluble platinochloride, and with alumina, a double sulphate having the crystalline form of common alum, with a similar composition. Dumas also classes it with the alkali-metals, because it is necessary to halve its atomic weight in order to make its atomic heat equal the atomic heats of other metals; and he gives calculations to prove that the atomic weights of thallium and the alkali-metals are numerically related. Another argument on this side of the question is, that thallium sometimes accompanies the alkali-metals in mineral waters; this, however, is no argument at all, as the same reasoning would prove that iron and most other metals belong to the same class.

In support of the view that thallium is one of the heavy metals, the following reasons may be given:—The argument from the alkaline character of the oxide applies both ways. The oxides of lead, silver, and mercury, are well known to be soluble in water, and communicate to it an alkaline reaction. This is not very marked, owing to their slight solubility, but there is little doubt that if we could find a neutral liquid which would dissolve either of those oxides in larger quantities, their alkaline character would become more apparent. Such a liquid, as Erdmann has pointed out, exists in a solution of neutral acetate of lead, which dissolves considerable quantities of oxide of lead, forming a solution as alkaline as that of oxide of thallium, and readily attracting carbonic acid from the air. Oxide of silver also appears to be more soluble in an aqueous solution of nitrate of silver than in pure water, and reacts more strongly alkaline. The slight affinity which oxide of thallium has for water, also shows it to be more allied to a heavy metallic oxide; it is not only non-deliquescent, but when its aqueous solution is evaporated even at the ordinary temperature over sulphuric acid in a vacuum, it gives up all its water and leaves the anhydrous oxide; it is difficult to conceive a more striking contrast to the behaviour of a true alkali under the same circumstances. The formation of an alum is considered by some authorities to be a strong argument in favour of the relationship of thallium to the alkali-metals. This argument falls to the ground now that Professor Church* has obtained a silver-alum crystallizing in octahedrons, and containing 24 equivalents of water. The insolubility of the double chloride of platinum and thallium has, in my opinion, no bearing whatever on its classification. The metal stands alone in this respect; platinochloride of thallium is almost as insoluble as sulphate of baryta, and in comparison with this, the platinum-salt of potassium may be called extremely soluble; whilst even the rubidium and cæsium salts must be regarded as soluble by the side of the thallium-salt. The fact of thallium having been obtained by Böttger, in conjunction with the alkalies in an analysis of a certain mineral water, is an accident, depending upon the special analytical process which he adopted.

Again, it is urged by Dr. W. A. Miller, that the chemical energy of the alkali-metals lithium, sodium, potassium, rubidium, and cæsium, increases in the order mentioned, which is that of their equivalents; whilst thallium, with a higher equivalent than any of these, shows a greatly diminished chemical activity. Numerical relations between atomic weights are of little account, for figures can be made to prove anything. I may, however, remark that Dumas uses in his calculations an old and now admittedly erroneous equivalent for cæsium (123 instead of 133), and that by similar processes of addition, multiplication, or subtraction, it would be easy to prove that thallium belonged to any desired group, especially the mercury, lead, and silver group.*

---

* Chemical News, March 26, 1864.

As further reasons for classing thallium with the heavy metals, may be urged the complete, or nearly complete insolubility of its peroxide, sulphide, phosphide, iodide, bromide, chloride, chromate, and phosphate; its ready reduction from aqueous solutions of its salts by metallic zinc; the highly poisonous character of its compounds; the production of a brown insoluble peroxide by electrolytic means; its high atomic weight; the complexity of its photographic spectrum, shown by Dr. W. A. Miller, to contrast strongly with the simplicity of those of the alkali-metals; its low conducting power for electricity, which is close to that of lead and of tin, and much inferior to that of the alkali-metals; its specific heat which coincides with that of lead; its density and melting point, very near those of lead; and, finally, its physical appearance and characters, which approach so nearly to those of lead, that few persons would notice at first sight any difference between the two metals.

## *Compounds of Thallium.*

### THALLIUM AND OXYGEN.

### A. *Oxide of Thallium*, TlO.

Thallium oxidises in the air with almost the rapidity of an alkali-metal. When freshly cut with a knife, the proper colour of the metal may be seen, rapidly assuming a yellowish cast, which increases until the metallic lustre is obscured by a dark grey film resembling the superficial tarnish of cadmium. After the surface is coated with a film of oxide, scarcely any further change takes place, and the metal may be freely exposed to the air. If it is exposed to damp air containing carbonic acid, a white crystalline powder of carbonate of thallium appears on the surface. Perfectly bright metallic thallium has no taste; a tarnished surface, on the other hand, has a caustic alkaline taste, leaving a metallic flavour on the tongue for some hours afterwards. The superficial tarnish consists of the protoxide containing a minute quantity of the peroxide. If the metal has been oxidised by exposure to the temperature of boiling water, rather more peroxide is formed, and when the heat is raised to the melting point of the metal, the protoxide which forms is mixed with a large quantity of peroxide. Thallium, when melted, behaves like lead, the oxide fusing like litharge; the fused oxide is absorbed by bone-ash, and a silver-thallium alloy can be cupelled like silver-lead. Thallium does not decompose pure water, either at the common temperature or when boiling; a piece of absolutely pure metal kept for nearly twelve months in a stoppered-bottle, under distilled water, had its metallic lustre undimmed; the sides of the glass were slightly turbid, and a few crystals of carbonate of thallium were apparent in the upper part of the vessel, the water reacting strongly alkaline. The oxygen was absorbed from the atmosphere. At a red heat the vapour of water is decomposed by thallium, with formation of oxide and separation of hydrogen, which burns with a green flame. Alcohol appears to be decomposed by the metal more readily than water.

---

* Eq Hg + Eq Pb = Eq Tl; Eq Ag + 2Eq Mb = Eq Tl.

The coating of tarnish forming on the surface of the metal is instantly removed by water. The oxide may be prepared by allowing granulated thallium to oxidise in warm moist air, and then boiling in distilled water. By repeating this operation two or three times, a saturated hot solution of the oxide is formed. Upon filtering, the small quantity of carbonate which may have formed separates at first in white needles, whilst, upon further cooling, the oxide crystallises out in yellow needles.

Anhydrous protoxide of thallium is formed by exposing these yellow crystals in a vacuum over sulphuric acid; it then forms a reddish-black mass, retaining the shape of the crystals. When heated to about the melting point of the metal, it melts to a brown limpid liquid, which, at a higher temperature, evolves reddish-brown vapours, partially oxidising at the same time to the peroxide. Upon cooling, the brown liquid solidifies to an almost black crystalline mass. The fused oxide attacks glass and porcelain, removing the silica. When heated, it always peroxidises slightly. Oxide of thallium is decomposed by hydrogen at a red heat, forming water and metallic thallium. The decomposition, however, is never perfect, owing to the oxide fusing and volatilising. When fused with sulphur, it forms sulphide of thallium, and in aqueous solution with metallic zinc, metal is precipitated, and oxide of zinc formed. When an electric current is passed through a solution of the oxide, it is also reduced to the metallic state.

*Combinations.* α. With water. α. HYDRATED OXIDE OF THALLIUM.

Hydrated oxide of thallium is prepared as above-described, or it may be obtained, as recommended by Lamy, by decomposing a solution of the sulphate with baryta-water, and evaporating the alkaline solution in a vacuum. This method is not so good as the one already described, owing to the large quantity of liquid required, and the great difficulty of getting the oxide free from baryta; it is, moreover, somewhat tedious. The best method of obtaining perfectly pure hydrated oxide of thallium, is to add water to the oily compound of oxide of thallium and alcohol. This at once separates the oxide in the form of a bright yellow crystalline mass, which may be separated from water and alcohol by exposure to warm dry air.

Hydrated oxide of thallium forms pale yellow, long, prismatic crystals, which lose water and become almost black and anhydrous by exposure to the temperature of a water-bath in air, or to sulphuric acid in a vacuum at the common temperature. On the addition of water, the dark oxide immediately becomes hydrated and yellow. It has a slight tendency to absorb oxygen, and after evaporation and re-solution, it always leaves a slight residue of peroxide.

β. AQUEOUS OXIDE OF THALLIUM. Protoxide of thallium is a powerful base, dissolving readily in water, and forming a colourless strongly alkaline solution. It has a slight odour, similar to that of potash, dissolves the skin, and feels greasy. It has a strong action on the hair and nails, staining them a deep and very permanent brown colour. It blues litmus paper, browns turmeric paper, has a metallic alkaline taste, and neutralises acids perfectly. It eliminates ammonia from chloride of ammonium, and reacts with hydrochloric acid, iodide of potassium, sulphide of ammonium, &c., in the characteristic manner of a thallium-salt. An aqueous solution of protoxide of thallium has a greater similarity to potash than to ammonia in its reactions with metallic salts. When added to solutions of salts of magnesium, cerium, manganese, zinc, cadmium, lead, iron (proto and sesqui), cobalt, nickel, copper, mercury, silver, and peroxide of thallium, it precipitates the respective oxides, without redissolving them in excess. From salts of aluminium and chromium it precipitates the hydrated oxides, and easily redissolves them when in excess, forming with alumina a solution unaltered by boiling, but precipitated by a current of carbonic acid, and with chromium a green solution precipitated on boiling.

*b*. With acids it forms the THALLIUM-SALTS. The affinity of oxide of thallium for acids is considerable. The salts are for the most part colourless, unless the acid itself is coloured. They are mostly soluble in water, are neutral to test-paper, and have a slight metallic taste. They are strongly poisonous, three or four grains of the sulphate being sufficient to kill a small animal; the symptoms are somewhat similar to those produced by lead. After working with considerable quantities of sulphate, in the extraction of the metal from flue dust, the hands become burnt, and the epidermis cracks in all directions, looking yellow and horny. In this respect it somewhat resembles a mercury-salt. The salts when ignited, generally fuse at temperatures below redness, and then volatilise; some salts, such as the sulphate and phosphate, will stand a bright red heat without change. On charcoal before the blow-pipe, they volatilise, communicating an intense green colour to the flame. Their aqueous solution is rapidly precipitated in metallic crystals by *zinc*, and slowly by *iron*. *Phosphuretted hydrogen* precipitates a black phosphide. *Hydrosulphuric acid*, added to a solution of oxide of thallium combined with a weak acid, such as carbonic or acetic, separates the whole of the metal in the form of a deep brown sulphide; from solutions of thallium-salts of the stronger acids, such as sulphuric or nitric acid, sulphuretted hydrogen precipitates nothing if the acid is in excess, and only a small portion of the metal if the solution is neutral. *Sulphide of ammonium* precipitates thallium-salts completely, the precipitated sulphide being insoluble in sulphide of ammonium, in caustic alkalis, their carbonates and cyanides, and only slightly soluble in acetic acid. In salts of the protoxide, *hydrochloric acid* and *soluble chlorides* precipitate a difficultly soluble white chloride; *hydrobromic acid* and *bromides* precipitate a white, nearly insoluble bromide; and *hydriodic acid* and *iodides* precipitate an insoluble yellow iodide. *Alkalies, alkaline carbonates*, or *bicarbonates* produce no change in thallium proto-salts; *phosphate of soda* gives a white precipitate, nearly insoluble in ammonia, easily soluble in acids. *Chromate of potash* gives a yellow precipitate of chromate of thallium, insoluble in cold nitric or sulphuric acid, but turned orange-red on boiling in the acid solution. *Bichloride of platinum* precipitates a very pale yellow insoluble double salt.

### B. *Peroxide of Thallium* $TlO_3$.

Peroxide of thallium is always formed when metallic thallium is heated, or even when a solution of the protoxide is evaporated in the air. When the metal is burnt in oxygen, the product is chiefly peroxide. This compound is best prepared by adding potash, ammonia (or even protoxide of thallium) to a solution of sesquioxide or peroxide of thallium; in either case the peroxide is precipitated, and must be washed and dried at a temperature of 500° F. Peroxide of thallium is also formed when a voltaic current from two cells of Grove's batteries is passed through a solution of sulphate of thallium, platinum terminals being used. If the solution is perfectly neutral, thallium slowly makes its appearance at the negative pole, whilst the positive pole becomes coated with a film, presenting at first the most brilliant colours of thin plates, and gradually increasing in thickness until it becomes a cake of peroxide of thallium. As the sulphuric acid accumulates in the liquid, the peroxide at first formed gradually dissolves. If the solution of sulphate of thallium is rendered alkaline with ammonia, the peroxide is formed in larger quantity, scaling off and falling to the bottom of the liquid as soon as it becomes of a certain thickness. If the sulphate of thallium is acid, oxygen is evolved, and no peroxide is separated; in this case it dissolves in the acid present.

Anhydrous peroxide of thallium is a dark brown powder, fusing with difficulty and evolving oxygen at a red heat, becoming reduced to the protoxide. It is neutral to test paper, and insoluble in water. It dissolves readily in sulphuric, nitric, and hydrochloric acid, forming hygrometric and instable salts.

Hydrated peroxide of thallium, $TlO_3.HO.$, is obtained by drying the precipitated peroxide at a temperature of 212° F.; it forms a brown powder, a shade lighter than the anhydrous oxide, and retains one equivalent of water. When formed in the wet way, it always appears to be hydrated. Reducing agents, such as sulphurous acid or oxalic acid, convert it to the lowest state of oxidation, forming sulphate or oxalate of the protoxide of thallium; in the latter case carbonic acid is evolved.

### THALLIUM AND HYDROGEN?

According to Dr. Herapath, when bismuth containing thallium is tested with a hydrogen-flame by Marsh's method in a darkened room, a brilliant green light is produced where the flame impinges on a white porcelain plate. This experiment has not been confirmed, and I have been unable to obtain any evidence of the existence of a compound of thallium and hydrogen. When zinc is added to acid solutions containing thallium, the metal is reduced, but the evolved hydrogen contains no thallium; and the same result is obtained when an alloy of thallium and zinc is dissolved in sulphuric acid. When hydrogen is passed over metallic thallium at a red heat, the metal volatilises, and is mechanically carried forward by the current of gas, communicating to the flame a brilliant green colour. The thallium, however, does not appear to be chemically united to the hydrogen, as it is gradually deposited as a dark powder upon the cold sides of the glass tube, although the flame still burns green after the gas has passed through six feet of cold tubing. This hydrogen flame burns with a bright green colour, and deposits a reddish brown mirror with a metallic lustre, upon a cold porcelain surface. This mirror has many points of resemblance to the one given by arsenic. Upon moistening it with sulphide of ammonium, it becomes rather darker in colour, but is not otherwise affected. An aqueous solution of chloride of lime dissolves the mirror readily. Upon exposing the deposit to the vapour of iodine, it turns permanently yellow, and, upon subsequent addition of sulphide of ammonium to the yellow iodide, the latter becomes of a dark, reddish brown colour, but does not dissolve. Upon strongly heating the glass tube through which the hydrogen containing thallium is passed, no metallic deposit is formed on the glass. The two former characters serve to distinguish the thallium mirror from antimony, whilst the two latter distinguish it from arsenic.

## THALLIUM AND CARBON.

*Carbonate of Thallium*, $TlO.CO_2$.—The film of oxide which forms upon the surface of metallic thallium when exposed to the air, gradually absorbs carbonic acid and becomes converted into carbonate, which frequently appears in the form of crystalline needles. A saturated aqueous solution of oxide of thallium absorbs carbonic acid rapidly and deposits carbonate of thallium in crystals. Carbonate of thallium may be prepared in quantity by allowing granulated [illegible] slightly moistened with water, to oxidise in a warm atmosphere. Upon boiling out with water containing an excess of carbonate of ammonia, and filtering, crystals of carbonate of thallium will be deposited as the solution cools. The first crop of crystals generally have a slight yellow tinge, owing to the presence of a trace of oxide or peroxide. Recrystallisation will render them perfectly white. Carbonate of thallium crystallises in long prismatic needles; they are perfectly white, have a brilliant appearance, are highly refractive and very heavy, resembling a salt of lead. The salt is anhydrous; its taste is mildly caustic and somewhat metallic, remaining on the tongue for a considerable time. When heated, it fuses much below redness to a clear liquid which solidifies to a dark grey crystalline mass. It may be kept fused for a considerable time without decomposition or loss of weight, but when heated to dull redness, it evolves white vapours, and bubbles of gas make their appearance. The specific gravity of the fused salt is 7·06 (Lamy). It is not very soluble in cold water; 100 parts of water at 60° F. only dissolve 4·02 parts; at 140° F. the same quantity of water dissolves 11·7 parts, and at the boiling point water dissolves 27·21 parts. The specific gravity of a cold saturated solution is 1037·7. M. Erdmann has said that carbonate of thallium has no alkaline reaction; to test this, a warm saturated solution of pure carbonate of thallium had a rapid stream of carbonic acid passed through it, until the liquid was quite cold and the excess of salt had crystallised out. Even then the solution was alkaline, both to turmeric and litmus paper, although the liquid contained an excess of carbonic acid gas, which was liberated from all parts when gentle heat was applied. Carbonate of thallium therefore is not only alkaline, but an excess of carbonic acid will not render it neutral. The crystals deposited from this carbonic acid solution were analysed by being dried over sulphuric acid in a vacuum. They lost no weight when heated to the melting point. The carbonic acid was determined in the usual manner, and the thallium by precipitation with platinum. The numbers agreed closely with the formula $TlO.CO_2$. Crystals of carbonate deposited from a solution containing an excess of carbonate of ammonia were found to have the same composition.

## THALLIUM AND BORON.

*Borate of Thallium.*—Boracic acid added to a solution of car-borate of thallium, or borax added to sulphate of thallium, precipitates a white granular borate of thallium, insoluble in excess of the precipitant and in cold dilute sulphuric acid; soluble in boiling water.

### THALLIUM AND PHOSPHORUS.

A. *Phosphide of Thallium.* Phosphuretted hydrogen passed through an ammoniacal solution of sulphate of thallium precipitates phosphide of thallium as a black insoluble powder, permanent in the air at common temperatures.

B. *Phosphate of Thallium.* A hot solution of nitrate of thallium is heated nearly to the boiling point, and glacial phosphoric acid added to it; upon neutralising with ammonia, a thick felt-like mass of crystals of phosphate of thallium is deposited. This salt is soluble in nitric acid, separating in large crystals. Lamy describes the phosphate as a soluble salt, like the carbonate; but experiment shows that 100 parts of water at 60° F. dissolve only 0·497 parts, and the same quantity of boiling water dissolves 0·6712 parts. The salt, dried over sulphuric acid in a vacuum, loses nothing but a minute trace of hygroscopic water, upon being heated to full redness for two hours in an open crucible. It melts below redness, forming a deep brown very mobile liquid, becoming as it cools dark orange yellow, then pale yellow, and, finally, solidifying to a highly crystal-white mass. The composition of the salt is most probably $3TlO.PO_5$, it cannot contain either water or ammonia, as it loses nothing at a red heat; on boiling it with nitrate of silver, the characteristic yellow phosphate of silver $3AgO.PO_5$ is instantly produced, the solution remaining neutral.

### THALLIUM AND SULPHUR.

A. *Sulphide of Thallium,* $TlS$.—From neutral solutions of nitrate, sulphate or chloride of thallium, sulphuretted hydrogen precipitates only a small portion of the metal, as a grey-black sulphide. If other metals are present which are completely precipitated by this gas, they carry down larger quantities of thallium. Solutions of acetate, oxalate, or carbonate of thallium are completely precipitated. Sulphide of ammonium precipitates all thallium-salts, forming a brownish black, dense, flocculent precipitate; if present in small quantities only, the minute particles of sulphide suspended in the liquid quickly collect together into a few large clots at the bottom of the vessel, leaving the solution quite clear. Sulphate of thallium projected into fused cyanide of potassium is reduced to the state of sulphide, forming in this case a brittle metallic-looking mass, of the lustre of plumbago, and fusing more readily than the metal. When precipitated in the wet way, the sulphide oxidises in the air, and whilst being washed, unless the washing-water contains a little sulphide of ammonium, a considerable quantity of the precipitate will be converted into sulphate of thallium, which passes through into the filtrate. After drying in hydrogen, it still oxidises on exposure to the air. According to M. Lamy, its specific gravity is 8. The higher compounds of thallium appear to be reduced to the state of protosulphide by ebullition with an excess of sulphide of ammonium. Precipitated sulphide of thallium is readily soluble in dilute sulphuric or nitric acid, and is insoluble in sulphide of ammonium or cyanide of potassium. Analysis shows that the composition is $TlS$, but the numbers did not agree within 0·5 per cent., owing to the difficulty of weighing sulphide of thallium without oxidation.

B. *Hyposulphite of Thallium.* When sulphate of thallium is added to hyposulphite of soda, a white curdy precipitate falls. This is soluble in boiling water, and separates in rhombic crystals on cooling. When it is boiled in a solution containing a slight excess of sulphate of thallium, a somewhat larger crystalline deposit is produced. When heated with an excess of hyposulphite of soda, it dissolves, with partial decomposition and production of brown flocks, but deposits no crystals on cooling. It is not soluble to any extent in a cold solution of hyposulphite of soda.

C. *Sulphate of Thallium.—a. Monobasic,* $TlO.SO_3$. Formed by dissolving thallium in dilute sulphuric acid. Hydrogen is evolved, and upon evaporation, the solution deposits crystals of the sulphate. It forms long, thin tabular crystals (right rhombic prisms, Lamy), very brilliant and colourless. Exposed to a dull red heat, they decrepitate slightly without fusing. At a bright red heat, they melt to a clear liquid, which, at a somewhat lower temperature, solidifies to a dirty yellow crystalline mass, gradually becoming lighter yellow, and finally, when cold, quite white. The total loss in an experiment in which the sulphate was kept at bright redness for eight hours was only 0·3 per cent., most of which went off at the first heating. The specific gravity of fused sulphate of thallium is

6·77 (Lamy). It dissolves in 21·1 times its weight of water at 60° F., and in 5·4 parts of boiling water, forming a neutral solution. The crystals contain no water of crystallisation; and upon analysis give numbers closely agreeing with the formula $TlO.SO_3$. The composition of the salt was found to be the same, whether it was crystallised from a slightly acid solution, or from an ammoniacal solution containing sulphate of ammonia. When sulphate of thallium is heated in a crucible with black flux or with cyanide of potassium, it is first reduced to the state of sulphide, and then to the metallic state. It is difficult, however, to remove all the sulphur in this way.

*b. Acid Sulphate.* When sulphate of thallium is heated with one atom of oil of vitriol, or when the chloride is decomposed with an excess of sulphuric acid, a bisulphate is formed, which is more fusible than the neutral sulphate, and at a red heat gives off anhydrous sulphuric acid, leaving the compound *a*.

D. *Sulphate of the Teroxide.* When teroxide of thallium $TlO_3$, is dissolved to saturation in slightly warm dilute sulphuric acid, and the solution is evaporated, a granular crystalline deposit of sulphate of teroxide of thallium is produced. This is very soluble in water containing a trace of free sulphuric acid, but when dissolved in pure water, it decomposes, with deposition of teroxide of thallium. When heated to redness, it melts, becomes yellowish, loses oxygen and sulphuric acid, and finally leaves a residue of ordinary sulphate of thallium.

## THALLIUM AND SELENIUM.

*Selenide of Thallium* is formed by fusing together equal equivalents of the two elements. It is very fusible, and of a greyish black colour (Lamy).

## THALLIUM AND IODINE.

*Iodide of Thallium*, TlI.—When the two elements are heated together, they combine, without evolution of light, and form the proto-iodide. The same compound is readily formed by double decomposition, between an alkaline iodide and a salt of the protoxide of thallium. It forms a beautiful yellow powder, rather darker than sulphur, fusible below redness, and yields a scarlet liquid, which, as the mass cools, remains scarlet for some time after it has solidified, and then suddenly changes to bright yellow.

When the precipitated and dried iodide of thallium is spread on paper with a little gum-water, it undergoes a similar, but opposite change to that experienced by iodide of mercury, upon application of heat. The yellow surface, when held over a spirit-flame, suddenly becomes scarlet, and will frequently remain so, after cooling, for several days. Hard friction with a glass rod changes the scarlet colour back to yellow. Iodide of thallium is very difficultly soluble in water, requiring 4453 parts of water at 63° F., or 842·4 parts of boiling water to dissolve it; it is slightly more soluble in an aqueous solution of iodide of potassium.

### Thallium and Bromine.

*Bromide of Thallium* is formed by adding thallium to bromine, the two bodies then combining, with evolution of heat. It is also produced by double decomposition. It forms a very pale yellow precipitate, fusible below redness. It is intermediate in solubility between the iodide and chloride.

### Thallium and Chlorine.

A. *Protochloride of Thallium*, $TlCl$.—Metallic thallium is attacked at the ordinary temperature by chlorine; when heated in the gas, it burns and forms a yellow liquid, which solidifies on cooling to a pale yellow or white crystalline mass. If excess of chlorine has been present, the product consists almost entirely of higher chlorides, but in presence of an excess of thallium, the white protochloride is the only compound formed. Boiling hydrochloric acid attacks thallium but slowly, the action soon ceasing, owing to the formation of a layer of difficultly soluble chloride of thallium. When hydrochloric acid, or a soluble chloride, is added to a solution of the protoxide of thallium or one of its soluble salts, a white curdy precipitate of protochloride of thallium is thrown down, scarcely to be distinguished at first sight from chloride of silver. When boiled in water, it dissolves like chloride of lead, and separates again on cooling; the crystals, however, are much smaller and less brilliant than those of chloride of lead. One part of the chloride dissolves in 283·4 parts of water at 60° F., and in 52·5 parts of boiling water. It is insoluble in alcohol, and scarcely, if at all, more soluble in aqueous ammonia, cyanide of potassium, or hydrochloric acid, than it is in water. When boiled in nitric acid or aqua regia, it is converted into a higher chloride.

It may be heated to a temperature of 500° F., without loss of weight; at a slight increase of heat, it suddenly melts to a thin brown liquid, white vapours being simultaneously evolved. On cooling, it solidifies to a white crystalline mass, somewhat resembling horn-silver, possessing a brilliant lustre, but being only slightly flexible. The specific gravity of the fused chloride is 7·02 (Lamy). The fused lump is reduced to the metallic state by zinc and dilute acid, like fused chloride of silver. According to Lamy, chloride of thallium is unalterable by light; experiment, however, shows that it undergoes a considerable darkening when exposed either to sunlight or diffused daylight. Protochloride of thallium is also precipitated when sulphurous acid, or an alkaline sulphite, is added to one of the higher chlorides of thallium.

B. *Sesquichloride of Thallium.*—$Tl_2Cl_3$. This compound is prepared by dissolving the metal or the protochloride in nitro-hydrochloric acid. On cooling it separates in yellow crystalline scales. It may also be prepared by heating the terchloride till it fuses, and no more chlorine is evolved. When heated it melts below redness, forming a dark brown liquid, which solidifies to a lighter coloured mass. Sesquichloride of thallium is soluble in 380·1 times its weight of water at 60° F., and in 52·9 parts of boiling water. Pure water produces a slight decomposition into teroxide and protochloride, which, however, may be prevented by the addition of a drop of nitric or hydrochloric acid. When slowly crystallised from slightly acidulated boiling water, it separates in brilliant orange-yellow hexagonal plates, considerably darker than when it is obtained by more rapid crystallisation, and presenting the closest resemblance to iodide of lead. Sesquichloride of thallium is also precipitated by the cautious addition of sulphite of soda to one of the higher chlorides. Whenever it separates from a liquid, it shows remarkable crystalline characters, and when just precipitated, it produces a magnificent satiny lustre in the liquid. Ammonia, potash, or even a solution of oxide of thallium, added to the sesquichloride, produces instant decomposition into teroxide and protochloride, according to the following equation:

$$2Tl_2Cl_3 + 3NH_4O = TlO_3 + 3TlCl + 3NH_4Cl.$$

When pure dry ammoniacal gas is passed over the sesquichloride, heat being applied with a spirit-lamp, the salt first assumes a deep orange tint, without fusing, and loses its brilliant, almost metallic lustre. On increasing the heat, the chloride fuses, and at the same time chloride of ammonium vapours are abundantly evolved. The melted compound froths up, and assumes a deeper tint, ultimately becoming brown, and then gradually paler, until there finally remains perfectly white protochloride of thallium.

The reaction between ammonia and sesquichloride of thallium is represented by the following equation:—

$$3Tl_2Cl_3 + 4NH_3 = 6TlCl + 3NH_4Cl + N.$$

C. *Bichloride of Thallium* is formed by carefully treating either thallium or the protochloride in a slow current of chlorine, the resulting chloride being kept liquid. This bichloride is pale yellow, rather hygrometric, and decidedly more fusible than the sesquichloride. It is reduced by heat to the sesquichloride (Lamy).

D. *Terchloride of Thallium.*—The terchloride is formed by dissolving the teroxide in hydrochloric acid, or by acting upon thallium or a lower chloride, with a large excess of chlorine, at a gentle heat. It is white, crystalline, and deliquescent, melting with the greatest facility, and almost immediately decomposing, with loss of chlorine (Lamy). It is converted by heat into the sesquichloride.

E. *Chlorate of Thallium.*—$TlO.ClO_5$. This salt may be prepared by dissolving the metal in chloric acid, a very gentle heat being employed, or by mixing together saturated aqueous solutions of chlorate of potash and nitrate or acetate of thallium. It forms a beautiful difficultly soluble salt, crystallising in long needles; it is anhydrous, easily fusible, and readily decomposed by heat.

When the chlorate is heated with an excess of chloric acid, the crystals dissolve; the liquid turns yellow; oxygen-compounds of chlorine are evolved; and when the solution is evaporated to a syrupy consistence, small brilliant colourless crystals are deposited, which are instantly decomposed when water, alcohol, or ammonia is added, with production of the brown teroxide of thallium. The salt is remarkable for its immediate decomposition in the presence of water. If the colourless crystals are allowed to remain for a minute exposed to the ordinary atmosphere, they turn dark and blacken instantly when breathed upon, evolving a strong chlorous odour. A drop of water placed on the filtering paper in which the crystals have been dried, instantly blackens it. I have not satisfactorily determined the composition of these crystals. When decomposed by ammonia, they yield 71·47 p.c. of hydrated teroxide of thallium, only very minute traces of thallium and hydrochloric acid being found in the filtrate. On first describing this salt, I assumed that it consisted of perchlorate of thallium with three atoms of water, and was resolved into hydrated teroxide of thallium, chloric acid, and two atoms of water. This would yield 71·62 per cent. of hydrated teroxide of thallium; but the same analytical result would be obtained on the assumption that the formula of the crystals was $TlO_3.ClO_5.3Aq$. This subject is now under further examination.

## THALLIUM AND NITROGEN.

Attempts have been made to prepare a nitride of thallium, but hitherto without success.

*Nitrate of Thallium.* $TlO.NO_5$.—Cold concentrated nitric acid scarcely affects thallium at all, but when diluted with its own bulk of water or warmed, it is acted upon violently, with evolution of nitric and nitrous oxide. No ammonia is produced in the reaction. As the liquid cools, an abundant crystallisation of nitrate of thallium takes place. The great bulk of this is nitrate of the protoxide, but it contains a small quantity of a persalt of thallium, which is not entirely removed by recrystallisation. It may be detected by adding a few drops of ammonia to the solution of the nitrate; a slight precipitate of hydrated teroxide of thallium will be produced, scarcely to be distinguished in appearance or colour from sesquioxide of iron. This impurity may be entirely removed by fusion. When the white crystals of nitrate of thallium are heated to a temperature of about 400° F., they melt to a clear liquid, a considerable amount of froth at first covering the surface, and gradually disappearing, until the liquid is quite clear, with the exception of a brown powder, consisting of teroxide of thallium, suspended in it. After cooling, the salt is perfectly soluble in water, with the exception of this brown powder, and the filtered solution deposits on evaporation brilliantly white crystals of pure nitrate of thallium.

The crystals when heated to a temperature of 394° F., melt to a liquid as clear and colourless as water. Fifty grains have been kept at a temperature of about 500° F. for six hours without appreciably losing weight. Upon cooling, the fused salt solidifies to a white opaque crystalline mass. Nitrate of thallium is soluble in 9·4 times its weight of water at 60° F., and in considerably less than its own bulk of boiling water, forming a syrupy solution. (Lamy states that 100 parts of boiling water dissolve 580 parts of the salt.) It separates on cooling in white prismatic needles, which are anhydrous and are insoluble in absolute alcohol. Its aqueous solution is neutral to test-paper.

### THALLIUM AND ALUMINIUM.

*Double Sulphate of Alumina and Thallium.—Thallium-alum.*— When equivalent quantities of sulphate of thallium and sulphate of alumina are mixed together and the solution is evaporated, brilliant and colourless crystals of thallium-alum are produced in large octahedra. These are identical in crystalline form with potash-alum (Lamy).

### THALLIUM AND CHROMIUM.

A. *Neutral Chromate of Thallium.*—When yellow chromate of potash is added to a neutral salt of the protoxide of thallium, and the mixture rendered slightly alkaline with ammonia, a pale-yellow precipitate is produced, very difficultly soluble in water, and yielding on analysis numbers which agree with the formula $TlO.CrO_3$.

B. *Bichromate of Thallium.*—On adding bichromate of potash to a neutral salt of protoxide of thallium, an orange-yellow precipitate is produced, which has the formula of bichromate of thallium.

C. *Terchromate of Thallium.*—Either of the above compounds, boiled with nitric acid, is converted into a brilliant orange-red compound, which, on analysis, gives results pointing to the formula of a terchromate. If the nitric acid be moderately strong and in large excess, either of the chromates is dissolved, and the solution, on cooling, deposits magnificent cinnabar-red crystals, which appear to be the compound C. This salt is one of the most insoluble of the compounds of thallium, requiring 2814 parts of cold water, and 438·7 parts of boiling water, to dissolve it. Sulphuric acid acts likes nitric acid. Hydrochloric acid dissolves the chromates readily, chlorine being evolved, and a soluble perchloride being produced.

When mixed with hydrochloric acid and alcohol, or with sulphite of soda, these compounds are quickly decomposed, protochloride of thallium being precipitated, whilst sesquichloride of chromium remains in solution. The former compound, being insoluble in alcohol, affords an easy means of analysis.

### THALLIUM AND MANGANESE.

These elements occur together in nature. Three years ago, before I had published anything respecting thallium, my friend Mr. C. Greville Williams, to whom I had sent a small portion of substance which showed the green line, wrote to me, in a letter dated March 10th, 1861, " I have a minute blowpipe specimen of pyrolusite, which gives your green line as distinctly as the residue sent by you. I enclose half my specimen." In consequence of this, an immense number of specimens of pyrolusite and similar minerals were examined, but as no other specimens were found to give the green line, the matter was allowed to drop. The above observation has now met with confirmation. Professor Bischoff, in a note to the number of the *Annalen der Chemie und der Pharmacie*, for March, 1864, announces the occurrence of thallium in a specimen of binoxide of manganese, but, like Mr. Williams, he has not succeeded in obtaining more than a small quantity of this mineral.

When manganese and thallium occur together in solution, the thallium may be separated by precipitation with iodide of potassium, sulphurous acid having previously been added to reduce the metals to the state of proto-salts.

### THALLIUM AND BISMUTH.

These elements frequently occur together in minerals containing bismuth, and thallium may frequently be detected in medicinal preparations of bismuth, especially the carbonate. Dr. W. Bird Herapath says that when a solution of bismuth containing thallium is introduced into a hydrogen apparatus, the resulting gas will contain a volatile thalliuretted hydrogen, which burns with a green flame. I have already referred to this subject in a previous part of this paper, and have been quite unable to detect thallium in bismuth by this means. There are very delicate analytical processes for detecting thallium in bismuth. The bismuth-salt is to be first obtained in the form of a dilute solution, any convenient acid being used for this purpose. A slight excess of carbonate of soda is now added, and then a little cyanide of potassium free from sulphide. The mixture is to be gently warmed, and allowed to stand for ten minutes, then filtered, and a few drops of sulphide of ammonium added to the clear liquid. If the slightest trace of thallium were originally present in the bismuth-compound, it will now be precipitated as a sulphide, which, upon gently heating the liquid (not to the boiling-point), gradually collects together in deep brown, almost black flakes, after the characteristic manner of sulphide of thallium.

This process is one of extreme delicacy; by means of it one part of thallium can be detected in the presence of more than 100,000 parts of bismuth. In some cases, the thallium is present in so small a quantity as to occasion only a slight darkening of the liquid when the sulphide of ammonium is added. Upon allowing this to digest at a gentle heat, it will generally collect in the form of a few flakes at the bottom. These may be collected together on a small filter, washed to the apex, and tested in the spectroscope. When the precipitate is only present in sufficient quantity to produce a faint dark stain on the filter-paper, the latter may be partially dried by pressure between blotting-paper, opened, and the stained surface scraped up with a knife. The dark fibres are now to be twisted up in a platinum wire loop, and held in the flame of the spectroscope, when they will give abundant indications of the presence of thallium.

## THALLIUM AND ZINC.

I have met with many specimens of blende and calamine, especially from Nouvelle Montagne and the neighbourhood of Spa, in Belgium, in which thallium was present in tolerable quantity. In such cases it accompanies the zinc in most of its preparations, and may, therefore, be frequently detected in the commercial metal. By proceeding in the following manner, the black residue which is left behind when zinc is dissolved in sulphuric acid will generally be found to contain thallium. The residue is dissolved in nitric acid; the solution evaporated with excess of sulphuric acid; the residue dissolved in a small quantity of water; the liquid filtered from sulphate of lead; and sulphite of soda added. Iodide of potassium will now precipitate the thallium.

## THALLIUM AND CADMIUM.

These two metals frequently occur together. The thal[illegible] be detected by adding bichromate of potash, and [illegible] or with sulphite ammonia to the acid solution of these metals: [illegible]sed, protochloride of mate of thallium will then be precipitated. Commercial sulphide of cadmium, as sold for artists' use, varies considerably in tint, some specimens being of a much deeper orange than others. I have frequently found thallium in the dark-coloured varieties, and it is therefore probable that the variations of colour in sulphide of cadmium are due to traces of thallium. As an instance of a highly thalliferous sulphide of cadmium, I may especially mention a beautiful specimen from Nouvelle Montagne, which formed a prominent object in the Belgian Department of the Exhibition of 1862.

## THALLIUM AND TIN.

An alloy of thallium and tin is readily obtained by fusion under cyanide of potassium or coal gas. With 5 per cent. of thallium, the alloy is perfectly malleable. When these two metals occur together in a liquid, they may be separated by adding an excess of sulphide of ammonium to the alkaline solution. Sulphide of thallium will be precipitated, whilst the tin will remain in solution.

## THALLIUM AND LEAD.

These two metals readily melt together, forming a malleable alloy. In analytical operations, they may be separated like thallium and bismuth; or the lead may be precipitated as sulphate, whilst the sulphate of thallium will remain in solution. Sulphuretted hydrogen in an acid solution will also precipitate the lead, and leave the thallium dissolved.

## THALLIUM AND IRON.

Certain kinds of iron pyrites constitute the richest source of thallium hitherto met with. At the commencement of this paper, I have fully described the methods of separating thallium from thalliferous pyrites on the large scale. The new metal may be readily detected in thalliferous pyrites in the following manner:—Dissolve the finely powdered mineral in nitro-hydrochloric acid; evaporate with excess of sulphuric acid until the nitric acid is evolved; dissolve in water; and add sulphite of soda to reduce the iron and thallium to the state of proto-salts. On adding a little iodide of potassium, and allowing the liquid to stand for some time, a bright yellow precipitate of iodide of thallium will separate. This test is sufficiently delicate to show thallium in a pyrites which does not contain more than 1 part in 10,000. I have frequently found thallium when working upon no more than ten grains of pyrites.

### THALLIUM AND COPPER.

It is difficult to make an artificial alloy of thallium and copper containing much of the former metal. When thallium is projected into a crucible containing melted copper, it boils, and in great part volatilises, some however uniting with the copper. By repeated additions of thallium, I have succeeded in forming a hard, brittle, white alloy. With a still smaller quantity of thallium the mixture is gold-coloured; and with 95 per cent. of copper, it forms a hard button, flattening somewhat under the hammer, but soon cracking at the edges. In small quantities, thallium appears to diminish the malleability and ductility of copper. Copper prepared in Spain by the cementation process already described at the commencement of this paper, frequently contains considerable quantities of thallium. A specimen kindly lent me by Dr. Matthiessen, which had a conducting power for electricity of about 15, that of pure copper being 100, was found to contain a large quantity of thallium: it is probable that the pre-eminently bad quality of this copper is to be thus accounted for. When the two metals occur together analytically, they may be easily separated by adding to the acid solution sulphurous acid in excess, and then iodide of potassium; a dirty white precipitate will fall, consisting of subiodide of copper and iodide of thallium. On adding ammonia to the washed precipitate, the iodide of copper rapidly dissolves, with absorption of atmospheric oxygen, to a deep blue liquid, whilst the iodide of thallium is left behind as an insoluble yellow powder. Sulphuretted hydrogen in an acid solution also separates the copper, but as metallic sulphides are very liable to carry down sulphide of thallium, I prefer using other means of separation, if sulphuretted hydrogen can be avoided.

### THALLIUM AND MERCURY.

The two metals unite readily, forming a solid crystalline amalgam. I have found no process better for separating them analytically than by the use of sulphuretted hydrogen. From per-salts of mercury the gradual addition of iodide of potassium effects a ready separation. If much mercury is present, the precipitate is almost pure scarlet, but on further addition of iodide of potassium, drop by drop, the iodide of mercury dissolves and leaves the insoluble yellow iodide of thallium.

### THALLIUM AND GOLD.

*Double Chloride of Thallium and Gold.*—When a hot aqueous solution of chloride of thallium is mixed with a slight excess of chloride of gold, brilliant gold-coloured crystals are deposited, which increase as the solution cools; these consist of a double chloride of gold and thallium. They are difficultly soluble in water, and at a red heat leave an alloy of gold and thallium.

### THALLIUM AND PLATINUM.

A. *Alloy of Thallium and Platinum.*—These two metals combine together with incandescence. If a piece of metallic thallium is placed on a platinum wire-loop, and held in the flame of a spirit-lamp, they rapidly melt together, becoming nearly white hot, and evolving abundant fumes of thallium; the resulting alloy is highly crystalline, very hard, and almost as brittle as glass. The most convenient way of obtaining the green light of thallium is to alloy a platinum wire-loop in the above manner. When this is introduced into a spirit lamp, or heated before the blowpipe, a green tint of extraordinary splendour is communicated to the flame.

B. *Double chloride of Thallium and Platinum.*—This salt is precipitated in the form of a very pale yellow crystalline powder when bichloride of platinum is added to an aqueous solution of a salt of the protoxide of thallium. When heated to redness, it leaves an alloy of thallium and platinum, the latter metal continually volatilising, until, after being kept for some time at nearly a white heat, the platinum is almost free from thallium. This is the most insoluble salt of thallium I have yet met with, one part requiring no less than 15585 parts of water at 60° F., or 1948 parts of boiling water to dissolve it. The great insolubility of this compound having been considered a reason for classing thallium with potassium, it may be of interest to compare it with the corresponding potassium, ammonium, rubidium, and cæsium salts. It will be seen that its degree of solubility gives it very little relationship to these metals.

| One part of Chloroplatinate of— | Water at 60° F. | Boiling water. |
|---|---|---|
| Potassium dissolves in | 108 parts | 19 parts. |
| Ammonium „ „ | 150 „ | 80 „ |
| Rubidium „ „ | 740 „ | 157 „ |
| Cæsium „ „ | 1308 „ | 261 „ |
| Thallium „ „ | 15585 „ | 1948 „ |

## ORGANIC COMPOUNDS OF THALLIUM.

Thallium appears to have some tendency to form organic compounds; only a very limited number have, however, been as yet prepared. Its compounds with organic acids are, for the most part, colourless, except the ferrocyanide and the picrate; they are soluble in water, and generally crystallise with remarkable facility.

*Formate of Thallium* is prepared by dissolving carbonate of thallium in formic acid; it is very soluble in water, and melts without decomposition below 212° F.; its composition is $C_2HTlO_4$ (Kuhlmann).

*Cyanide of Thallium* is obtained by mixing a concentrated solution of cyanide of potassium with a saturated solution of carbonate of thallium, or by neutralising oxide of thallium with hydrocyanic acid (Kuhlmann). It is more easily prepared by mixing together strong solutions of cyanide of potassium and nitrate of thallium. It separates in brilliant crystalline plates, not very soluble in water. When heated, the salt decrepitates and fuses easily. When intensely heated on platinum foil, it volatilises without reduction or alloying with the platinum.

*Ferrocyanide of Thallium.*—This salt is precipitated by mixing ferrocyanide of potassium with nitrate of thallium. It forms yellow crystals, slightly soluble in water.

*Cyanate of Thallium* is obtained by mixing alcoholic solutions of cyanate of potash and acetate of thallium. It is precipitated in small brilliant plates, very soluble in water and very slightly soluble in alcohol (Kuhlmann).

*Sulphocyanide of Thallium.*—This is a very beautiful salt; it is precipitated by adding sulphocyanide of potassium to a soluble thallium salt. (The per-salts are reduced by it to proto-salts). It falls as a dense crystalline and brilliantly white powder which, when crystallised from hot water, forms brilliant prisms sometimes two inches long.

*Ethylate of Thallium.*—Absolute alcohol is decomposed by thallium, with evolution of hydrogen, when the two are heated together in a sealed tube in a water-bath (Church). When pure thallium in a finely divided state (and partially oxidised on the surface) has absolute alcohol poured over it, the spirit becomes slightly opalescent. In the course of a few hours, this opalescence disappears, and needle-shaped crystals, together with a few drops of a colourless heavy liquid, form in the alcohol. After standing with partial exposure to the air for some days, the thallium dissolves in quantity, and a considerable amount of the oily liquid accumulates. The supernatant alcoholic liquid is unaffected by dilution with water, and acts in every respect like a strong solution of protoxide of thallium. The oily liquid is a compound of protoxide of thallium and alcohol; it is decomposed upon the addition of water, solidifying to a yellow crystalline mass of protoxide of thallium, which dissolves on further addition of water and heating. It makes a greasy stain upon paper, and is almost insoluble in alcohol. Lamy prepares it by dissolving protoxide of thallium in alcohol and evaporating on a water-bath; he describes it as a heavy oily liquid, not boiling at 212° F. Its specific gravity is 3·5, and its refracting power is almost as great as that of bisulphide of carbon.

*Acetate of Thallium.*—This salt is prepared by dissolving carbonate of thallium in a slight excess of glacial acetic acid, and evaporating to dryness over a water-bath. The residue is then gently heated on a sand-bath, till it fuses, and no more odour of acetic acid is perceptible. The fused mass is dissolved in water, filtered from a small quantity of a dark precipitate which is usually formed, and then gently evaporated over the water-bath. The salt separates in long silky prisms or plates of a pearly lustre. When heated in an air-bath, they undergo no change until the temperature rises to 240° F., when they fuse to a colourless oily liquid, no evolution of gas or other decomposition taking place. Upon cooling, the liquid solidifies to a mass of white radiating crystals, having a beautiful satiny lustre. They bear an hour's exposure to a temperature of 340° F. without decomposition, but at a slightly higher temperature, an empyreumatic odour is observed, and the mass on solidifying becomes slightly brown.

The crystals are anhydrous when dried over sulphuric acid at the ordinary temperature; they have no odour of acetic acid; they deliquesce in a cold damp atmosphere, but are permanent in ordinary dry air; they are very soluble in water and alcohol, and crystallise from the latter with great facility. Their aqueous solution will bear ebullition without loss of acetic acid. Sulphuretted hydrogen instantly precipitates the metal as sulphide. Upon analysis the crystals yielded numbers closely agreeing with the formula $C_4H_3TlO_4$.

*Oxalate of Thallium.*—This salt is readily prepared by boiling together equivalent quantities of carbonate of thallium and oxalic acid, in just sufficient water to dissolve the product when hot. Upon cooling, oxalate of thallium crystallises out in the form of small prisms, brilliantly white and lustrous. It may also be prepared by mixing together saturated aqueous solutions of nitrate of thallium and oxalate of ammonia. The salt bears a temperature of 400° F. without change. At 480° F. it becomes slightly discoloured, but scarcely loses any appreciable weight. Upon ignition the crystals decompose, leaving a residue of oxide and metal. They are not very soluble in water and are insoluble in alcohol. One part of the salt requires 69·3 parts of water at 60° F. and 11 parts of boiling water to dissolve it. Hydrochloric acid poured over the dry crystals converts them into a porous spongy mass of chloride. Analyses show that the formula of the salt is $C_2TlO_4$. Kuhlmann has analysed it with the same result.

*Binoxalate of Thallium.*—On boiling together two equivalents of oxalic acid and one of carbonate of thallium, the binoxalate is deposited, on cooling, in the form of large plates, having a pearly lustre, and containing water of crystallisation, which is driven off at a temperature of 270° F.; the formula of the dried salt is $C_4HTlO_8$. The hydrated crystals appear to be slightly efflorescent, and contain two atoms of water of crystallisation. One part dissolves in 18·7 parts of water at 60° F., and in less than its own bulk of boiling water, forming a syrupy solution; it is strongly acid to test paper.

*Malate of Thallium* crystallises with difficulty; it is deliquescent and melts below 212° F. (Kuhlmann).

*Tartrate of Thallium.*—The neutral tartrate is deliquescent and crystallises with difficulty. It is slightly soluble in water and alcohol. The crystals are anhydrous; heated to 338° F., they carbonise; at a higher temperature, they leave a mixture of a yellow oxide and a little reduced metal. The formula is $C_8H_4Tl_2O_{12}$ (Kuhlmann).

*Bitartrate of Thallium* is precipitated in a crystalline form when tartaric acid is added to a solution of neutral tartrate of thallium. Its composition is $C_8H_5TlO_{12}$ (Kuhlmann).

*Tartrate of Thallium and Antimony.*—When oxide of antimony is treated with a solution of bitartrate of thallium, a double salt is produced, moderately soluble in water, crystallising in needles and efflorescing when dried (Kuhlmann).

*Paratartrate of Thallium* is very soluble in water, and yields groups of crystals, which appear to belong to the prismatic system. Its composition is $C_8H_4Tl_2O_{12}$ (Kuhlmann).

*Urate of Thallium* is almost completely insoluble, and is obtained by double decomposition between urate of potash and carbonate of thallium (Kuhlmann).

*Valerate of Thallium* has the greatest analogy to the acetate, and, like it, is very soluble in water and in alcohol. Its formula is $C_{10}H_9TlO_4$ (Kuhlmann).

*Picrate of Thallium* crystallises in silky plates resembling crystals of picrate of potash (Kuhlmann).

*Citrate of Thallium* is very deliquescent, and crystallises with difficulty. It is slightly soluble in alcohol; its composition is $C_{12}H_5Tl_3O_{14}$ (Kuhlmann).

*Benzoate of Thallium* crystallises in pearly plates, and is not volatile (Kuhlmann).

*Thallium-benzamide.* This compound has been examined jointly by Professor Church and the author. It is prepared by adding pure benzamide to a hot aqueous solution of pure protoxide of thallium. The benzamide dissolves freely, and the excess crystallises out on cooling. Upon adding a large excess of absolute alcohol to the filtrate, thallium-benzamide is immediately precipitated. This body crystallises in fine needles, soluble in both hot and cold water, forming a highly alkaline solution. Its insolubility in alcohol affords a ready means of purification both from benzamide and from oxide of thallium. When heated, it melts without decomposition, at a higher temperature becoming dark coloured, and evolving white inflammable vapours, which burn with a smoky flame tinged with green. At a red heat, all organic matter is dissipated, a fusible residue of oxide of thallium being left behind. Its composition is

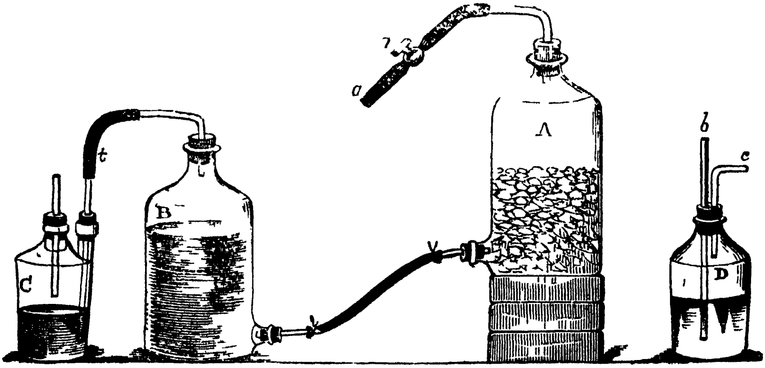
$$\left.\begin{matrix}C_{14}H_5O_2\\ Tl\\ H\end{matrix}\right\}N.$$

It has many properties in common with its analogues, argento- and mercuro-benzamide, although, as might have been anticipated from the peculiarities of its metallic ingredient, it differs from them in several particulars. Hydrochloric acid, added to the compound, occasions an immediate precipitate of chloride of thallium, benzamide being separated at the same time.

## XVII.—*Description of a New Apparatus for producing Sulphuretted Hydrogen.*

By Dr. Phipson, F.C.S., &c.

Having lately seen in the laboratory of Professor Pisani, of Paris, a very simple and effective apparatus for evolving sulphuretted hydrogen, and passing it through a metallic solution, without exposing the operator to the disagreeable and noxious effects of the gas, I beg to submit a description and drawing of the apparatus (kindly given to me by M. Pisani) to the notice of the Chemical Society.



A is a bottle (with two tubulures) containing sulphide of iron; it is placed upon three bricks, and communicates, by means of two short glass tubes and a caoutchouc tube, with the bottle B, which is filled with hydrochloric acid.

In the figure, the apparatus is supposed to be at rest, and the little brass stopcock *r*, belonging to the bottle A, is closed, whilst the bottle B communicates with the tubulated bottle C, containing ammonia. In this position the acid, which, we will suppose, has acted upon the sulphide of iron, has run out of the bottle A into B, and any gas remaining or generated in the apparatus by the acid which still adheres to the sulphide of iron, can only escape through B into the ammoniacal liquid in the bottle C, where it forms hydrosulphate of ammonia. Now, when the apparatus is at work, the ammonia-bottle C is taken away, the stop-cock *r* is opened, and the bottle A, being taken off the bricks, is placed on a level with the bottle B, which causes the acid to run on to the sulphide of iron and disengage sulphuretted hydrogen; the caoutchouc tube *a*, of bottle A is united to the flask D (which contains the metallic solution to be acted upon by the gas) by means of the tube *b*, whilst the bent tube *c* of the bottle D, is made to communicate with the ammonia solution C, by means of the caoutchouc tube *t*. In this position the gas, after traversing the metallic solution in D, is entirely absorbed by the ammonia solution, forming hydrosulphate of ammonia.

The advantages of this apparatus are: first, that it prevents all odour of sulphuretted hydrogen in the laboratory; secondly, that the excess of gas is employed to manufacture a constant supply of sulphide of ammonium, a reagent frequently required; thirdly, that as soon as the operation is terminated, the whole of the hydrochloric acid is withdrawn from the sulphide of iron; and, fourthly, its simplicity. An ordinary washing-bottle can be inserted, if necessary, between A and D when the apparatus is in activity.

## XVIII.—*On Nitro-compounds.* (Part I).

By Edmund J. Mills, B.Sc., F.C.S.

The large and important group of substances known as "nitro-compounds" has always been admitted to a considerable share of the attention of chemists. The ease with which these bodies can be formed and reduced, the varied products to which they give rise on reduction, their critical value in the establishment of rational formulæ, are circumstances which may well account for the interest felt in them both by the purely scientific and the commercial experimenter. It has, accordingly, been to me a matter of some surprise that they have not hitherto been submitted to a systematic investigation, either with the view of classifying them in a satisfactory manner, or of solving some of the very obscure but attractive problems which they present.

The following paper contains a detailed account of some experiments still in progress, in which I have endeavoured to bear both the above objects in mind. As a means of obtaining results capable of being used as a basis of classification, no method held out better promise than that of reduction—a process, indeed, to which the majority of nitro-compounds had been already submitted. But, since the labours of chemists had not been directed by an intention similar to the present, and had shown that a change of the reducing agents, or a difference in the mode of applying a single one, has a material influence on the product of the reaction, I determined to acquire new data by acting on a number of typical nitro-compounds with one reducing agent, taking care to keep the circumstances of the reduction as uniform as possible. For this purpose I have selected hydriodic acid—a reagent which, in the hands of Lautemann and others, has become so distinguished in value and interest. We owe to Gay-Lussac[*] the examination into its action on nitric acid, and to Lautemann[†] the recent inquiry into its behaviour with picric acid. The liquid and solid compounds thus treated are as follow:

### 1. *Chloropicrin.*

This substance, the discovery of Stenhouse, and having the well-known formula—

$$C(NO_2)Cl_3$$

was observed by Geisse[‡] to yield methylamine when submitted to Béchamp's process. He thus expresses the reaction:—

$$C(NO_2)Cl_3 + 12H = CH_5N + 2H_2O + 3HCl$$

It was natural to expect a similar result from the employment of hydriodic acid—

$$C(NO_2)Cl_3 + 12HI = CH_5N + 2H_2O + 3HCl + 12I.$$

---

[*] Gmelin's Handbook, Watts's translation. Vol. ii., pp. 263, 396.

[†] Ann. Ch. Pharm. cxxv. 1.

[‡] Ann. Ch. Pharm. cix. 282.

Accordingly chloropicrin (the purity of which had been ascertained by a chlorine determination) was sealed up with fuming hydriodic acid. A very slight alteration was apparent, even in the cold, on standing several days; but when digested in the water-bath for four-and-twenty hours, it was evident that the contents of the tubes had undergone a powerful reaction. On cooling, iodine crystallised out in abundance. There was a slight report on opening the tubes; the liquid they contained, separated from the free iodine, to a great extent, by filtration, furnished, on evaporation to dryness, crystals of hydriodate of *ammonia*. After twice recrystallising, the purity of the latter substance was ascertained by an iodine determination.

0.30275 grm. substance, dried over oil of vitriol, furnished 0·4918 grm. iodide of silver.

In 100 parts.

| | Experiment. | Theory. |
|---|---|---|
| Iodine | 87·86 | 87·58 |

The crystals contained no methylamine. Geisse, on the other hand, obtained a product perfectly free from ammonia. The reaction may be thus written—

$$C(NO_2)Cl_3 + 6HI = NH_3 + CO_2 + 3HCl + 6I.$$

Besides qualitatively verifying this, I have determined the amount of ammonia produced.

0·6795 grm. substance, after treatment as above, and conversion of the ammonia into platinum-salt in the usual manner, gave 0·4008 grm. platinum, corresponding to 10·13 per cent. of ammonia.

| Experiment. | Theory. |
|---|---|
| 10·13 | 10·33 |

I attempted a quantitative determination of this kind, but without success, by heating the mixture in an oil-bath to 125°C. The operation was very soon terminated. Small white crystalline plates were visible at the top of the tube. They were readily soluble in alcohol, and probably consist of chloride of carbon. A temperature of 100°C. seems the most advantageous for the proper performance of the reaction.

### 2. *Marignac's Oil.*

This compound, known also as the chloride of dinitromethylene, which not only by the formula

$$C(NO_2)_2Cl_2$$

but also in type and character, is most closely connected with the preceding, was next submitted to treatment. It had been prepared by my friend, Mr. Walter Stewart, in accordance with Marignac's directions, and its purity was ascertained as in the previous case. A quantity of the oil was placed, together with some hydriodic acid, in a stout tube, through which a slow and constant current of carbonic anhydride was kept passing. The tube was surrounded with water, which could be gradually heated, and the gas proceeding from it was conducted, by means of a cork and an evolution-tube, into an upright glass cylinder (filled partly with potash-solution and partly with mercury) placed over a pneumatic trough. The sp. gr. of the hydriodic acid used, was about 1·58. The attack, as indicated by the elimination of free iodine, appeared to commence at nearly 60° C., but unabsorbed gas was not given off till the temperature of the bath was 94° C. This seems to indicate an intermediate stage in the reaction, which I may at once express thus—

$$C(NO_2)_2Cl_2 + 7HI = NH_3 + H_2O + 2HCl + 7I + (NO + CO_2).$$

Into the cylinder containing the unabsorbed gas, excess of oxygen was first introduced (when great absorption took place), and subsequently pyrogallic acid. In every operation there was a variable quantity of residual gas, very readily soluble in water, and consisting of nitrous oxide. In this respect, therefore, hydriodic acid resembles hydrosulphuric acid; for there can hardly be any doubt that nitric oxide is first eliminated and then reduced partially. The amount of ammonia produced was ascertained as in (1).

0·69550 grm. substance furnished 0·38725 grm. platinum = 9·59 ammonia per cent.

| Experiment. | Theory. |
|---|---|
| 9·59 | 9·71 |

The other products of the reaction were only qualitatively determined. Very many attempts, with this and other nitro-compounds, to determine the free iodine when nitric oxide has been evolved, have convinced me that in such a case the method of Bunsen is inapplicable.

### 3. *Dinitro-octylene.*

If, as Kekulé has done,* we view the compounds just discussed as more immediately connected with marsh-gas, it becomes interesting to inquire in what manner a nitro-derivative directly obtained from an olefiant, will behave with hydriodic acid. Accordingly, I have availed myself of dinitro-octylene, one of the important products obtained by Bouis,† when investigating the nature of castor-oil. The octylene was prepared by the action of chloride of zinc on octylic alcohol, and its derivative

$$C_8H_{14}(NO_2)_2,$$

by the treatment of the former with a mixture of sulphuric and nitric acids, and subsequent washing with distilled water.

A mixture of dinitro-octylene and hydriodic acid of sp. gr. 1·50, becomes homogeneous on shaking, and blackens, with formation of octylene and ammonia, below 100° C. At the same time a heavy oil is produced, probably consisting of the compound

$$C_8H_{16}.HI,$$

and this sometimes to so great an extent that the characteristic odour of the olefiant is not perceptible. It is necessary to use the freshly-prepared substance in this experiment; for the nitro-compound, if long kept, becomes altered, with the formation of certain products of a most rancid odour, which, on heating with hydriodic acid, evolve small quantities of nitric oxide.

I have only to add that, in preparing the dinitro-octylene, I have noticed, in small quantity, the white, crystalline body mentioned by Bouis.—For treatment, the substance was dried for a fortnight over oil of vitriol.

0·56175 grm. substance, heated with hydriodic acid, in a sealed tube, for a few hours to 100° C., gave 0·57155 grm. platinum = 17·47 per cent. ammonia. The equation

$$C_8H_{14}(NO_2)_2 + 16HI = C_8H_{16} + 2NH_3 + 4H_2O + 16I$$

---

* Ann. Ch. Pharm. ci. 204 (1857).

† Ann. Ch. Phys. [3] xliv. 77.

requires 16·83 per cent.

### 4. *α-Trinitro-glycerin.*

Desirous of witnessing the behaviour of an alcohol-derivative with hydriodic acid, I prepared trinitro-glycerin* for this purpose. Heated with the acid (of the sp. gr. last-mentioned) to a point which I was unable accurately to fix, but which lay considerably below 90° C., trinitro-glycerin is decomposed with great rapidity, yielding glycerin and nitric oxide, but no ammonia. The nitric oxide evolved is tolerably free from nitrous oxide:

$$C_3H_5(NO_2)_3O_3 + 9HI = C_3H_8O_3 + 3H_2O + 3NO + 9I.$$

### 5. *Nitro-benzol.*

It was impossible to omit the aromatic analogue of marsh gas from this list. Perfectly pure nitro-benzol, long heated to 100 ° C., with ordinary weak hydriodic acid, suffers no change. But I have ascertained that when it is heated with six times its volume of hydriodic acid of sp. gr. 1·44, in a tube 13·3 mm. in diameter, with frequent agitation, complete opacity of the hydriodic acid takes place at 104° C. The product of the reaction is aniline in the state of hydriodate, perfectly free from the ammonia which is not unfrequently liberated in the application of Béchamp's process (Scheurer-Kestner). The aniline-salt thus obtained seemed to differ in no respect from that which arises in the contact of common aniline with hydriodic acid. It yielded, moreover, the following result on analysis:

0·2900 grm. substance, dried over sulphuric acid, gave 0·3093 grm. iodide of silver, = 57·64 per cent. iodine.

| Experiment. | Theory. |
|---|---|
| 57·64 | · 57·47 |

### 6. *Hexnitro-mannite.*

This substance may be taken as the best defined of those highly replaced compounds which are obtained by treating the members of the saccharine group with a mixture of sulphuric and nitric acid. It was prepared and purified in the usual manner. Treated with strong fuming hydriodic acid, hexnitro-mannite is readily attacked, with evolution of heat and nitrous fumes. The temperature, in two experiments, rose from 22° C. to 30° C. When heated in a water-bath to 81° C., with hydriodic acid of sp. gr. 1·603 at 17° C., as mentioned in (2), the latter became opaque; at a somewhat higher temperature, the development of nitric oxide took place with great regularity. The gas was contaminated with a small quantity of nitrous oxide. The deep brown liquid obtained when the reaction had terminated was boiled for some time with carbonate of lead, in order to volatilise the free iodine and convert the remaining hydriodic acid into iodide of lead. The solution was cooled, filtered, evaporated to dryness on the water-bath and extracted with hot alcohol, whence regenerated mannite* separated on cooling. I was unable to notice any difference between the mannite thus obtained, and that which had not been submitted to nitration. Twice crystallised, and dried at 100° C., it gave the following result on combustion:

---

* Professor Church, some time since, communicated to me a fact which he had observed—that trinitro-glycerin gradually loses its well-known explosive properties, the loss being accompanied with the formation of oxalic acid. I have verified this observation, which will be more closely examined hereafter. Meanwhile, the new compound may be termed *β*-trinitro-glycerin, and the explosive variety, *α*-trinitro-glycerin.

0·3734 grm. substance, furnished 0·5354 grm. carbonic anhydride and 0·2629 grm. water.

| | Theory. | | Experiment. |
|---|---|---|---|
| $C_6$ | = 72 | 39·56 | 39·11 |
| $H_{14}$ | = 14 | 7·69 | 7·82 |
| $O_6$ | = 96 | 52·75 | — |
| | 182 | 100·00 | |

In this reduction no ammonia is produced, but I have found that there is a small quantity of a secondary body found, which becomes brown on exposure to a heat 100° C. Other experimenters, also, when investigating nitro-compounds of this class, have observed that more than one reaction takes place when they have submitted them to reduction. The following equation, therefore, though representing a part of what takes place, does not, strictly speaking, include the whole:

---

* The regeneration of mannite from its nitro-compound was effected by Dessaignes (Compt. rend. xxxiii. 462) by means of sulphide of ammonium; the nitro-compounds of melampyrin, cellulose, and erythromannite have been reduced, in like manner, by Eichler, Béchamp, and Stenhouse respectively.

$$\underset{\text{Nitromannite.}}{C_6H_8(NO_2)_6O_6} + 18HI = C_6H_{14}O_6 + 6H_2O + 6NO + 18I.$$

### 7. *Nitraniline.*

The two modifications of this substance, known as $\alpha$ and $\beta$ nitraniline, the discoveries of Hofmann and Muspratt,* and of Arppe† respectively, have long been distinguished as furnishing one of the most remarkable cases of isomerism we possess. Accordingly, I have subjected them to the action of hydriodic acid, with the view of ascertaining whether the employment of this reagent would assist in solving this long-investigated problem.—The $\alpha$-nitraniline was prepared by the action of sulphide of ammonium on dinitro-benzol; the $\beta$-nitraniline by the action of potash on nitro-acetanilide‡. Both substances were dried at 100° C., and analysed.

*$\alpha$-nitraniline.* 0·2865 grm. substance gave 0·5477 carbonic anhydride and 0·1179 grm. water.

*$\beta$-nitraniline.* 0·51575 grm. substance gave 0·98725 grm. carbonic anhydride and 0·21450 grm. water.

| Theory. | | | Experiment. | |
|---|---|---|---|---|
| | | | | $\beta$ |
| $C_6$ = | 72 | 52·17 | 52·14 | 52·39 |
| $H_6$ = | 6 | 4·35 | 4·57 | 4·62 |
| $N_2$ = | 28 | 20·29 | — | — |
| $O_2$ = | 32 | 23·19 | — | — |
| | 138 | 100·00 | | |

The fusion-points were also taken, and compared with those obtained by other observers:

| | $\alpha$ | $\beta$ |
|---|---|---|
| Hofmann and Muspratt .... | 110° C. | — |
| Arppe .................... | 108° | 141° |
| Mills...................... | 110°·5 | 142°·2 |

---

* Ann. Ch. Pharm. lvii, 201.

† Ann. Ch. Pharm. xc, 147.

‡ Hofmann, Ann. Ch. Pharm. cxxi, 281

Either of these substances, when boiled with hydriodic acid of various strengths, gave rise to a separation of free iodine and the hydriodate of a base, doubtless the corresponding phenylene-diamine.* The hydriodates are splendid salts, probably colourless when pure, and differing in a marked manner in their solubility in hydriodic acid, the $\beta$-hydriodate being very little soluble, while the $\alpha$-hydriodate dissolves with ease. The $\beta$-hydriodate crystallises in broad, flat rectangular plates, with the lustre of mica; the $\alpha$-hydriodate in small plates, not so well defined or beautiful as those of the $\beta$-salt. It appeared to be of considerable interest to ascertain whether the two nitranilines were attacked at the same or different temperatures. The hydriodic acid employed had been heated, either with phosphorus or zinc-amalgam, and distilled not long before the experiment. The substance, dried at 100° C., was weighed in a tube of small dimensions, which was introduced into a wide test-tube of about 1·5 times its diameter, and 5 c. c. of hydriodic acid were then added. A thermometer was inserted into the liquid, and supported by a cork (pierced with an additional aperture), so as to occupy the axis of the large tube. The temperature at which the cylindrical portion of the mercury in the bulb ceases to be visible was carefully noted.† I term this, for convenience sake, the "*attack-point.*" In taking a pair of observations, it is necessary that the observer's eye, the centre of the apparatus, and some fixed object, should be in the same straight line in each case. I have used the same apparatus in every experiment, and find that accuracy is easily obtained with a little practice. On contact with hydriodic acid, $\beta$-nitraniline usually dissolves in the cold, while $\alpha$-nitraniline requires moderate heating to effect its solution.

All the circumstances of the experiments being otherwise alike, the only source of error appears to be the presence of free iodine, which, existing even to a very small extent in the hydriodic acid used, appears to lower both attack-points,—that of the $\beta$-nitraniline points more especially; which, indeed, is in accordance with the observation of Hofmann,‡ that the base obtained from this substance, in presence of an oxidising agent, produces violet and blue colouring matters with great facility. Hence, in the results mentioned below, the attack-point of β-nitraniline is probably in every case under the truth. Indeed, on two occasions I have in this way obtained altogether opposite results.

---

* Hofmann, Compt. rend. lvi, 21.

† A bath of oil of vitriol, the upper surface of which was level with the hydriodic acid, was employed in each experiment.

‡ Loc. cit.

The following are selected from a considerable number of experiments:—

Internal Diameter of Tube, 16·51 m.m.
Hydriodic Acid used, 5 c.c.

| Weight of Substance. | Sp. gr. of HI. | α-attack. | β-attack. | Difference. |
|---|---|---|---|---|
| 0·25 grm. | 1·441 | 94°·4 C. | 98°·3 C. | 3°·9 C. |
| 0·25 „ | 1·449 | 93°·3 | 97° 2 | 3°·9 |
| 0·30 „ | 1·462 | 93°·9 | 96°·6 | 2°·7 |
| 0·30 „ | 1·529 | 82°·8 | 93°·9 | 11°·1 |
| 0·30 „ | 1 603 | 81°·7 | 92° 8 | 11°·1 |

Hence β-nitraniline is attacked at a higher temperature, and consequently with greater difficulty than α-nitraniline. The weaker the acid, the higher is the attack-point; with very strong acid I have found they are identical, or rather undistinguishable, as might have been expected. A range of weight in the substance employed of 0·15 grm. to 0·30 grm. makes no difference in the attack-point.

It may be safely asserted that any nitro-compound, when mixed with hydriodic acid of sp. gr. 1·7, and heated to 100° C., is decomposed, with the conversion of its nitryl $(NO_2)'$ into $(NH_2)'$, or else into $(NO)'$. Using for the last two groups the names "amide" and "nitrosyl" respectively, we may arrange nitro-compounds in two leading divisions *according to their products of reduction*, viz., "Amido-gens," and "Nitroso-gens," with an intermediate group of "Amido-nitroso-gens." The substances discussed in the above paper will then be arranged as follows;

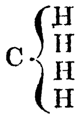
*Amidogens.*
Chloropicrin.
Dinitro-octylene.
Nitrobenzol.
{ α-nitraniline.
{ β-nitraniline.

*Amido-nitrosogens.*
Marignac's oil.

*Nitrosogens.*
Nitric acid.
{ α-Trinitroglycerin.
{ β-Trinitroglycerin ?
Hexnitro-mannite.

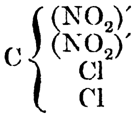
a list which, from the representative nature of the bodies it contains, might, without doubt, be very considerably extended in each of its divisions. It is so easy to decide, in most cases, to which class a given nitro-compound belongs, that a few minutes' examination only need be now necessary to ascertain whether it will yield a base or otherwise.

On comparing together the reactions described in (1) and (2), it is to be noticed what a striking difference is presented by two bodies precisely similar in type, and remarkably like each other in all their physical properties.



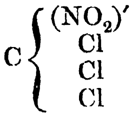
$$C\begin{cases} H \\ H \\ H \\ H \end{cases}$$

Marsh-gas.



$$C\begin{cases} (NO_2)' \\ (NO_2)' \\ Cl \\ Cl \end{cases}$$

Marignac's oil.



$$C\begin{cases} (NO_2)' \\ Cl \\ Cl \\ Cl \end{cases}$$

Chloropicrin.

Only one equivalent of nitryl in Marignac's oil behaves like the single equivalent contained in chloropicrin. Hence there must be two isomeric forms of nitryl,[*] the one yielding nitrosyl, the other amide, when reduced as I have indicated.

If nitro-benzol be converted into aniline, then into acetanilide, nitro-acetanilide, and lastly nitraniline, we perceive that the phenyl-residue $(C_6H_4)''$ is the same, formally, throughout these changes. Again, if some of the same nitro-benzol be converted into dinitrobenzol, and this into nitraniline, we see still that the phenyl-residue is unaltered. Moreover, since we have not yet an isomer of aniline, or, at any rate, one which affects the present argument, it follows that these isomeric aniline-derivatives are not to be accounted for by the existence in them of two kinds of amide $(NH_2)'$. We are, therefore, forced to the conclusion that, in the two nitranilines, we have two kinds of nitryl present. In the circumstance of attack-point this reasoning is experimentally established. The only substances to which the elimination of iodine can there be due, are, nitryl and hydriodic acid; but, as the hydriodic acid is the same in both cases, it follows that the dual nature of nitryl must be the cause of the isomerism. I have no doubt that the two kinds of dinitro-phenyl obtained by Fittig[†] are also to be accounted for in this manner, and I consider that α-and β-phenylene-diamine contain amide of two kinds, derived from the two kinds of nitryl. The following are some of the formulæ I have adopted:—

---

[*] Mills, Chem. News (1863), No. 183. Two forms *poly*-meric with each other are believed to exist by Playfair and Wanklyn. (Trans. Roy. Soc. Edin. xxii, 462.)

[†] Ann. Ch. Pharm. cxxiv, 285.

$\overset{\prime\prime}{C}_6H_4(\alpha NO_2)'(NH_2)'$
α-nitraniline.

$\overset{\prime\prime}{C}_6H_4(\beta NO_2)'(NH_2)'$
β nitraniline.

$\overset{\prime\prime}{C}_6H_4(\alpha NH_2)'(NH_2)'$
α-phenylene-diamine.

$\overset{\prime\prime}{C}_6H_4(\beta NH_2)'(NH_2)'$
β-phenylene-diamine.

When we reflect that isomeric phenyl-compounds, with scarcely an exception, contain nitrogen, we may expect to find the dual nature of nitryl, ere long, producing results of very wide application. Meanwhile I am continuing this examination, and am in hopes of obtaining a compound of nitryl, analogous to chloride of acetyl, whose nitryl may be thus transferred to a hydrocarbon unchanged; in this manner I trust to be able to fix the kind of nitryl that may be present in any nitro-compound.

I desire to express my best thanks to Professor Anderson for the use of his laboratory.

## XIX.—*On the non-Metallic Impurities of Refined Copper.*

By F. A. Abel, F.R.S.

The extent to which the various impurities, metallic and non-metallic, contained in copper when first reduced from its ores, are eliminated by the refining processes to which the metal is submitted, and the influences exerted by them, individually or when associated, upon the physical properties of copper, are matters which have from time to time engaged the attention of metallurgic chemists, and have formed the subjects of some very interesting and instructive researches. But, although most valuable information with regard to these questions has been contributed by Berthier, Karsten, and more recently by Percy, Dick, Matthiessen, and others, they are still open to investigation in many directions, and very numerous experimental data yet require to be furnished, before a clear understanding can be arrived at regarding the conditions, chemical and physical, by which many peculiarities in the properties of commercial copper are determined.

For some years past I have been occupied in studying the character of the numerous varieties of refined copper which have passed through my hands, and in endeavouring to obtain as precise a knowledge as possible of their chemical composition.

Although the methods in use for detecting and determining the proportions of the *metallic* impurities in the coppers of commerce have, many of them, been far from fully satisfactory, yet we do already possess considerable and trustworthy information with regard to the description of metals usually associated with commercial copper, and the general extent of their elimination by refining processes. Our knowledge relating to the *non-metallic* constituents of commercial copper has, however, been, up to the present time, of a much less definite and satisfactory character; and, although the interesting experiments instituted by Percy, and other chemists working at his instigation, have furnished valuable data regarding the tendency of copper to combine with and retain particular non-metallic elements, and the influence which these exert separately upon the properties of the metal, the information published up to the present time respecting the *non-metallic* elements which exist in the coppers of commerce, is still scanty and imperfect; a circumstance which may in great part be ascribed to the considerable difficulties experienced in arriving at trustworthy methods for determining the proportions of these elements, which are generally contained only in minute quantities, in a specimen of copper.

In a paper by Mr. Field and myself, recently published in the Journal of this Society, an account was given of methods, which considerable experience had shown to be trustworthy, for determining the proportions of the most important metals associated with copper, together with some of the results which, in the last few years, had been obtained in the application of these methods to the examination of coppers of commerce by ourselves, and by my assistant, Mr. E. O. Brown.

In the present communication I propose to submit to the Society an account of results obtained during a course of experiments extending, with frequent interruptions, over several years, the special object of which was to arrive at definite and trustworthy information with regard to the non-metallic impurities existing in refined copper, and which, therefore, were principally devoted to the establishment of satisfactory methods of detecting and estimating the proportions of non-metallic elements in copper. I believe that one or two of the methods which have thus been elaborated or modified present points of novelty, and that I am warranted in placing full confidence in the trustworthiness of the results which they have furnished, when applied to the examination of specimens of commercial copper, and of specimens specially prepared from copper, containing only very minute traces of metallic impurities.

### 1. *Oxygen in Copper.*

The extreme readiness with which copper is oxidised at elevated temperatures, and the considerable solubility of suboxide of copper in the fused metal, are well-known facts; and the results hitherto obtained by the qualitative examination of commercial copper, warrant the assertion that there hardly exists a specimen which, when heated in a current of dry hydrogen, will not furnish abundant evidence that it contains oxygen.

In an interesting paper published in 1856 by Dick upon the metallurgy of copper, several determinations of the proportion of oxygen (or of suboxide of copper) in specimens of that metal, are described as having been made by submitting a known weight of the heated metal for some time to the action of a current of dry hydrogen, and weighing the water produced. Three other methods were tried by Dick for ascertaining the proportion of oxygen in copper, of which two consisted in determining the loss of weight sustained by the copper, upon its fusion under charcoal, and in an atmosphere of hydrogen; while, by the third, a known weight of copper was converted into oxide by the wet way, and the difference between the weight of metal calculated from this oxide and the weight of the original metal, was taken to represent the proportion of oxygen contained in the latter. Not one of the above methods is, however, put forward by Dick as furnishing more than approximations to the proportion of oxygen in copper. Serious sources of error connected with the three last methods are specially pointed out by Dick, and he also shows that the discrepancies between results obtained in separate operations from one specimen of copper, by the first method, are great enough to deprive it of any claim to accuracy. Percy, in his valuable work on Metallurgy, for which Dick's experiments on the above and other matters of importance connected with the metallurgy of copper were instituted, does not refer to any more recent or satisfactory experiments on the determination of oxygen in copper; he appears, however, to incline to the opinion that, by employing the metal in a much finer state of division than as used by Dick, its treatment with hydrogen, and the estimation of the oxygen as water, might furnish uniform and exact results.

The uncertain and generally unsatisfactory nature of results obtained by me some years ago, in attempts made to arrive at the proportion of oxygen in commercial copper by its estimation in the form of water, induced me to take up the search for some trustworthy method for the quantitative examination of copper for oxygen. A long series of experiments, instituted with the valuable co-operation of Mr. E. O. Brown, during which several methods of apparent promise were necessarily abandoned as uncertain, terminated in the elaboration of a process which, having tested it rigidly and employed it extensively, I feel warranted in bringing forward with confidence as a trustworthy and sufficiently accurate method for determining the proportion of oxygen contained in copper.

It is advisable that the description of this method should be preceded by a brief account of a series of very carefully conducted experiments, recently instituted under my guidance by my assistant, Mr. F. H. Hobler, the results of which confirmed the correctness of the conclusion arrived at by me before the publication of Dr. Percy's work, that trustworthy indications of the proportion of oxygen existing in a specimen of copper, could not be furnished by treatment of the metal with hydrogen.

The arrangement of apparatus employed in these experiments was as follows:—The hydrogen passed, from an apparatus in which it was disengaged continuously, firstly, through a saturated solution of hydrate of soda; secondly, through a long tube filled with freshly-dried chloride of calcium. It then entered a tube eighteen inches long, filled with small fragments of fine copper wire, which, during the operations, was maintained at a red heat throughout its length, by means of a gas-furnace. From this tube the gas passed through two U tubes, the first containing pumice-stone moistened with sulphuric acid, the second being filled with fragments of hydrate of potassa. The gas, purified by passing through the above apparatus, entered a glass tube containing the copper to be examined, which was heated in a small gas-furnace, and, finally, escaped through the weighed chloride of calcium tube at the extremity of the apparatus. The connections between portions of the apparatus were very carefully made with india-rubber tubes and selected corks.

It was thoroughly established in the first instance, by blank experiments, that the chloride of calcium-tube suffered no appreciable increase in weight by the passage of hydrogen through the apparatus for two hours, the tube filled with copper wire being maintained at a red heat. In one blank experiment, the tube intended to receive the copper under examination was filled with fragments of glass and heated for two hours, during the continuous passage of hydrogen, which had previously been transmitted uninterruptedly through the apparatus for several hours. In this instance, the chloride of calcium-tube exhibited a very slight increase in weight (0·015 grains), which was to be ascribed to traces of air retained by the glass fragments. The above increase in weight was, however, very minute, as compared with those obtained in individual operations, in the subsequent experiments. The quantity of copper operated upon in the experiments varied between 300 and 500 grains. The metal was cut into pieces weighing from five to ten grains each; it was carefully washed, first with dilute nitric acid, then repeatedly with distilled water; lastly, it was dried by being maintained for a sufficient time at a very moderate heat in a current of hydrogen. The specimens operated upon, when thus cleaned, always presented a perfectly bright appearance.

A large number of separate experiments were instituted; the following will sufficiently illustrate the nature of the results obtained:

*Experiment* 1.—461·4 grains of a specimen of Kapunda copper, which, by the method to be presently described, had furnished 0·128 p. c. of oxygen (or 1·142 per cent. of suboxide of copper), were exposed for two hours to a continuous current of hydrogen, at a red heat, the gas having been passed through the apparatus for three hours before heat was applied. The water collected in the chloride of calcium tube was equivalent to 0·086 p. c. of oxygen or 0·767 p. c. of suboxide of copper in the specimen.

*Experiment* 2 was conducted, under precisely the same conditions as the first experiment, with 508·9 grains of the same copper, and furnished 0·091 p. c. of oxygen or 0·81 p. c. of suboxide of copper.

*Experiment* 3.—A specimen of copper, specially treated with the view of purifying it completely from oxygen, was next operated upon. The metal was melted in a Hessian crucible enclosed within a second, so that an intervening space was obtained, which was closely filled with finely-divided charcoal. The surface of the metal was covered with a thick layer of powdered charcoal, the crucibles were tightly closed and the metal was maintained in fusion under these conditions for an hour. It was afterwards allowed to cool down completely before the crucibles were opened. The copper thus treated, when examined for oxygen by the new method, was found to be free from that element.

302·38 grains of this copper were exposed for three hours at a red heat, to a current of hydrogen, the gas having been previously passed through the apparatus for three hours. The increase in weight of the chloride of calcium tube corresponded to 0·126 p. c. of oxygen, or 1·124 p. c. of suboxide of copper.

*Experiment* 4.—Although the blank experiments instituted in the first instance with the apparatus, were considered to have afforded conclusive evidence that no appreciable proportion of an increase of weight, sustained by the weighed chloride of calcium tube, could be ascribed to the escape of any water formed in the purifying tube filled with copper wire, beyond the U tubes which contained sulphuric acid and hydrate of potassa, the apparatus was so far modified for this and subsequent experiments, as to substitute for those U tubes a bulb-tube, containing anhydrous phosphoric acid and cotton wool. The connection of this tube with that containing the assay, was established by means of a single glass tube and corks, the exposed portions of which were carefully coated with sealing-wax. By thus abolishing the india-rubber connection first employed in this part of the arrangement, all possibility of the entrance of minute portions of the external air into the apparatus, between the final drying tube and the heated tube containing the assay, was removed.

The same specimen of copper employed in Experiment 3, was replaced in connection with the apparatus; a slow current of hydrogen was passed through the latter continuously for fifteen hours, and the copper was then heated in the current for two hours. At the expiration of that period, the chloride of calcium tube was detached and weighed, the passage of gas through the apparatus being allowed to continue during this operation. An increase in weight had been sustained by the tube, corresponding to 0·061 p. c. oxygen, or 0·544 p. c. of suboxide of copper in the metal treated. A further increase in weight, equal to 0·041 p. c. of oxygen or 0·366 p. c. of suboxide of copper, was obtained upon replacing the chloride of calcium tube, and again heating the specimen for one hour; and a third treatment for the same period furnished an additional quantity of water corresponding to 0·003 p. c. of oxygen or 0·268 p. c. of suboxide of copper. The current of hydrogen was stopped after this fourth hour's treatment.

*Experiment* 5.—Hydrogen was again passed continuously for about twenty hours through the apparatus and over the same specimen of copper employed in the two preceding experiments. At the expiration of that period, the specimen was heated in the current of gas, first for two hours and afterwards for one hour, the hydrogen passing uninterruptedly through the apparatus during the successive weighings of the chloride of calcium tube. The increase in weight of the latter, after the two hours' treatment, corresponded to 0·018 p. c. of oxygen or 0·161 p. c. of suboxide of copper, and, after the third hour to 0·006 p. c. of oxygen or 0·054 of suboxide of copper. After the second heating the current of gas was accidentally interrupted.

*Experiment* 6.—After hydrogen had passed through the apparatus for 15 hours, the same specimen of copper was exposed to a current of the gas at a red heat for 2·5 hours. The chloride of calcium tube was again found to have sustained an increase in weight, corresponding in this instance to 0·03 p. c. of oxygen, or 0·268 p. c. of suboxide of copper in the specimen.

*Experiment* 7.—The bulb-tube containing phosphoric acid, employed in the preceding experiments for the purpose of retaining any water formed in the tube containing heated copper wire, furnished, at their conclusion, but slight evidence of the absorption of moisture. In re-constructing the apparatus for this and the following experiment, a chloride of calcium tube was substituted for the phosphoric acid tube. 500 grains of Kapunda copper, from the same specimen employed in experiments 1 and 2, were introduced into the apparatus; a current of hydrogen was passed for about 20 hours, and the specimen was then heated for successive periods, the current of gas being maintained uninterruptedly while the consecutive additions to the weight of the chloride of calcium tube were determined. The results obtained were as follow :—

| Duration of exposure to heat. | | Water collected. | | Equivalent to— |
|---|---|---|---|---|
| 1 hour | .. | 0·061 p. c. O. | .. | 0·544 p. c. $Cu_2O$. |
| 1 „ | .. | 0·024 „ | .. | 0·214 „ |
| 1 „ | .. | 0·018 „ | .. | 0·161 „ |
| 2 „ | .. | 0·026 „ | .. | 0·232 „ |
| 1 „ | .. | 0·016 „ | .. | 0·143 „ |
| 1 „ | .. | 0·020 „ | .. | 0·178 „ |
| | | 0·165 | | 1·472 |

As in the case of the specimen of copper used in experiments 3, 4, 5, and 6, the increase in weight of the chloride of calcium tube appeared likely to continue for an indefinite period; the experiment was therefore brought to a termination after the sixth treatment of the metal.

*Experiment* 8.—A fresh quantity of the same specimen of Kapunda copper, weighing 500 grains, was exposed, exactly as in the preceding experiment, to successive treatments with hydrogen at a red heat, the current being first passed for 20 hours, and continuing uninterruptedly throughout the experiment.

The results furnished by successive weighings of the chloride of calcium tube were as follow :—

| Duration of exposure to heat. | | Water collected. | | Equivalent to— |
|---|---|---|---|---|
| 1 hour | .. | 0·055 p. c. O. | .. | 0·491 p. c. $Cu_2O$. |
| 1 „ | .. | 0·042 „ | .. | 0·375 „ |
| 2 „ | .. | 0·062 „ | .. | 0·553 „ |
| 1 „ | .. | 0·017 „ | .. | 0·152 „ |
| 2 „ | .. | 0·033 „ | .. | 0·294 „ |
| 3·5 „ | .. | 0·014 „ | .. | 0·125 „ |
| | | 0·223 | | 1·990 |

*Experiment* 9. 276·9 grains of a specimen of dry copper obtained from Swansea, in which, by the new method, 3·78 p. c. of suboxide of copper had been discovered, was submitted to treatment with hydrogen, the gas having been previously passed for 20 hours. Only two weighings of the chloride of calcium tube were obtained, as, after the second heating of the copper, the current of hydrogen was accidentally arrested. The following were the results :—

| Exposure to heat for | Water collected. | Equivalent to— |
|---|---|---|
| 2 hours .. | 0·245 p. c. O. .. | 2·185 p. c. $Cu_2O$. |
| 1 hour .. | 0·061 „ .. | 0·544 „ |
| | 0·306 | 2·729 |

It appears from the results of the above and other experiments of the same kind which were instituted, that:

1. Something like uniformity of results may occasionally be obtained by heating separate specimens of the same copper for equal periods, and under conditions as nearly equal as possible, in a current of hydrogen; but that,

2. The increase in weight of the chloride of calcium tube can, at no period of even a long-continued operation, with the employment of every precaution to exclude sources of error, be regarded as solely due to the collection of water produced from oxygen *contained* in the copper.

The experiments instituted with a specimen of copper which had been freed from oxygen, showed that hydrogen, thoroughly purified from oxygen and moisture, when passed even for many hours through a tube containing a specimen of copper, so divided as to expose a considerable surface, does not effect the complete expulsion, nor, subsequently, the entire removal, in the form of water, of the traces of atmospheric oxygen obstinately retained by the copper. The blank experiments in which fragments of glass were substituted for the fragments of copper, showed that the mechanical retention of air by numerous particles of a smooth and perfectly compact substance was far less considerable than when the rough and porous particles of copper were employed; and, lastly, it appears that although the larger proportion of the oxygen contained in a specimen of copper may perhaps be abstracted during the first two or three hours' treatment, its complete removal from the metal, in the form of water, requires very long-continued exposure to the action of hydrogen.

The obvious conclusion to be drawn from the above circumstances is, that correct indications of the proportion of oxygen existing in a specimen of copper cannot be obtained by treatment of the metal with hydrogen.

The plan already referred to, which has, in my opinion, been conclusively established, by a very extensive series of experiments, as a trustworthy method for determining the proportion of oxygen in copper, is based upon the following facts: Suboxide of copper decomposes neutral nitrate of silver in solution, slowly in the cold and rapidly at the boiling temperature, and the principal result of the reaction is the production of an insoluble basic nitrate of copper. Therefore, when copper is converted into nitrate by means of neutral nitrate of silver, any suboxide which it contains is converted, by one equivalent of nitrate of silver, into two equivalents of protoxide; the excess of base thus presented to the nitric acid brings about the production of an insoluble basic salt of copper; and the basicity of the total quantity of this product, obtained in the reaction, is proportionate to the amount of suboxide of copper contained in the original specimen operated upon; or, in other words, the quantity of an acid which the basic salt of copper obtained will neutralise, is equivalent to the proportion of oxygen existing in the specimen of copper examined.

The method of applying these facts to the determination of oxygen in copper, consists, simply, in converting a known weight of copper into nitrate, by digestion with neutral nitrate of silver, collecting and washing the mixture of precipitated silver and basic nitrate of copper which has formed, digesting it for a sufficient period with a known quantity of sulphuric acid, and eventually determining the proportion of acid which has been neutralised. It was well established by experiment, that sulphuric acid was the most suitable acid to employ, and that a standard solution containing one part of monohydrated acid to one hundred parts of water, exerts no solvent action upon very finely precipitated silver, either when the metal alone is digested with the acid, or in the cold, when a nitrate is also present; though, under those circumstances, a small quantity of silver is dissolved, if the digestion takes place at 100°C. It was also sufficiently proved by experiment that the basic nitrate of copper was readily and completely acted upon by digestion in the cold with sulphuric acid, of the strength specified.

The details of the several steps in this process for estimating oxygen in copper, are as follow:—

A fragment, weighing five or six hundred grains, of the copper to be examined, is first thoroughly cleaned by being immersed for a few seconds in concentrated nitric acid, then rapidly washed and dried at a temperature not exceeding 100° C. The clean piece of copper, having been accurately weighed, is digested in the cold with a neutral solution of nitrate of silver, the quantity employed corresponding to about 400 grains of metallic silver. After the lapse of three hours, about 100 grains of the copper will have passed into solution; the remaining piece of metal, to which portions of suboxide of copper may often be seen adhering, is then removed from the liquid with a pair of bone forceps, and thoroughly washed with distilled water over the vessel in which the digestion has been performed. It is afterwards quickly dried, and its weight is determined; the difference between it and the original weight represents the amount of copper under examination. The mixture of precipitated silver, basic salt of copper, and possibly of suboxide of copper, is separated from the principal proportion of soluble copper-salt, first by decantation, and afterwards by washing upon a filter; it is then transferred to a beaker, the filter itself being added, if necessary. About one drachm of nitrate of silver* solution (of the strength indicated above) and a known quantity of standard sulphuric acid are added, and the mixture is allowed to digest for about thirty minutes, being frequently agitated. The metallic silver is then filtered off and completely washed, the filtrate and washings are collected in a capacious flask, and the excess of sulphuric acid present in the liquid is estimated by means of a standard solution of carbonate of soda, which is added until a permanent precipitate of basic sulphate of copper makes its appearance. The proportion of sulphuric acid which had been neutralised by the basic nitrate of copper, furnishes, by a simple calculation, the proportion of oxygen or suboxide of copper in the metal operated upon.†

A large number of determinations of oxygen in samples of refined copper, and of specimens specially prepared for examination, have been instituted by this method by Messrs. Brown, Reynolds and Hobler; the following numbers, which are not specially selected, will serve as illustrations of the accuracy of the method:

---

* This is added for the purpose of completing the action upon any suboxide of copper or minute particles of metallic copper removed from the piece of metal by the washing.

† The sulphuric acid employed contains 460 grains of monohydrated sulphuric acid in 35,000 grains of water, and the standard solution of carbonate of soda is made by dissolving 466 grains of the dry salt in 35,000 grains of water.

| No. of example. | | Percentage of— | |
|---|---|---|---|
| | | Oxygen. | Suboxide of Copper. |
| 1 | 1 | 0·24 | 2·140 |
| | 2 | 0·25 | 2·230 |
| 2 | 1 | 0·33 | 2·944 |
| | 2 | 0·29 | 2·586 |
| | 3 | 0·32 | 2·854 |
| 3 | 1 | 0·331 | 2·952 |
| | 2 | 0·329 | 2·934 |
| 4 | 1 | 0·205 | 1·828 |
| | 2 | 0·189 | 1·685 |
| 5 | 1 | 0·117 | 1·043 |
| | 2 | 0·125 | 1·113 |
| 6 | 1 | 0·32 | 2·854 |
| | 2 | 0·31 | 3·140 |
| 7 | 1 | 0·33 | 2·944 |
| | 2 | 0·32 | 2·854 |
| 8 | 1 | 0·243 | 2·168 |
| | 2 | 0·250 | 2·230 |
| 9 | 1 | 0·331 | 2·952 |
| | 2 | 0·329 | 2·935 |
| 10 | 1 | 0·205 | 1·828 |
| | 2 | 0·189 | 1·686 |
| 11 | 1 | 0·128 | 1·142 |
| | 2 | 0·128 | 1·142 |

The whole of the foregoing experiments were instituted with Kapunda copper, which was specially selected as the subject of examination for oxygen, and of experiments to be based upon the results, on account of its remarkable freedom from metallic impurities. In commencing a series of experiments with this particular description of copper, it was my intention to endeavour to throw some light upon the precise causes of the remarkable differences in the physical properties exhibited by copper at different stages of the Welsh refining process. I had hoped, by experiments on a moderate scale, to have successively investigated the influence exerted by different metallic and other impurities upon the properties of the copper, in the presence and absence of oxygen, and to have arrived, by an exhaustive system of research, at some elucidation of the phenomena exhibited by copper at different stages of the poling process, and of the causes of the very great differences in the properties of different kinds of copper, refined, practically, under the same conditions. I greatly regret that, after having frequently, during the last six years, attempted to resume these experiments, in which I have been as constantly interrupted by labours connected with my official duties, I have been compelled to relinquish the hope, at any rate at present, of prosecuting further this interesting research. I venture now to bring before the Society the somewhat fragmentary results, of a preliminary character, which have been arrived at in my attempts to carry out this investigation; because every well-established fact, in connection with this subject, however trifling in itself, may prove to bear importantly upon our proper understanding of that important branch of the metallurgy of copper to which these observations refer.

The proportion of suboxide of copper found in different ingots of Kapunda copper is shown, by the results above given, to be somewhat considerable in some instances, and to vary between the extreme limits of one and three per cent. An inspection of the several ingots in which the oxygen was determined, showed decisively that some general relation existed between the appearance presented by the upper surface of an ingot and the proportion of oxygen which it contained. Thus, among the specimens referred to above, all those which had been taken from ingots exhibiting depressions along the centre of their upper surfaces, contained the highest proportion of suboxide of copper; those ingots whose surfaces were quite free from these depressions, contained the smallest proportions of oxygen. This indication of the comparative richness in oxygen, afforded by the depressed surface of an ingot, was found to be fully borne out by the results of examination of numerous other ingots of Kapunda copper, some of which exhibited depressions upon their upper surfaces, while others were free from any such depressions. Specimens were taken for analysis from the upper and lower portions of these ingots, all superficial oxidation being carefully removed; and it was observed, in the case of the ingots which exhibited no depression, that the lower portions generally contained somewhat less of oxygen than the upper parts.

The following are the results obtained; the mean percentages being given, where, as in the above analyses, duplicate determinations were made:—

### *Ingots with sunken surfaces.*

| | Top of Ingot. Percentage of | | Bottom of Ingot. Percentage of | |
|---|---|---|---|---|
| No. | Oxygen. | Suboxide of Copper. | Oxygen. | Suboxide of Copper. |
| 1 | 0·291 | 2·595 | 0·295 | 2·631 |
| 2 | 0·232 | 2·069 | 0·233 | 2·078 |
| 3 | 0·231 | 2·061 | 0·229 | 2·043 |
| 4 | 0·221 | 1·971 | 0·237 | 2·114 |
| 5 | 0·279 | 2·489 | 0·290 | 2·587 |
| 6 | 0·221 | 1·971 | 0·191 | 1·704 |

### *Ingots with level surfaces.**

| | Top of Ingot. Percentage of | | Bottom of Ingot. Percentage of | |
|---|---|---|---|---|
| No. | Oxygen. | Suboxide of Copper. | Oxygen. | Suboxide of Copper. |
| 1 | 0·150 | 1·338 | 0·134 | 1·195 |
| 2 | 0·153 | 1·365 | 0·152 | 1·356 |
| 3 | 0·155 | 1·383 | 0·115 | 1·026 |
| 4 | 0·158 | 1·409 | 0·098 | 0·874 |
| 5 | 0·156 | 1·392 | 0·102 | 0·910 |
| 6 | 0·128 | 1·142 | 0·096 | 0·856 |

A careful comparison of the fractures of the ingots employed in the above experiments, did not afford any satisfactory indications of sharply-defined differences in the structure of the copper containing different proportions of oxygen. It was observed, however, that the ingots which contained most suboxide of copper exhibited a dull and very close fracture, of a colour and texture like those of dry copper; the fractured surfaces were generally very free from the glistening spots, which are due to vesicular structure, and exhibited strongly developed lines, affording an appearance similar to fibrous structure and extending from the lower surfaces and sides, at right angles with them, to a considerable depth into the ingot. This particular appearance was also sometimes exhibited, though to a less considerable extent, by the fractures of ingots (with level surfaces) which contained comparatively small proportions of oxygen; but such fractures were always brighter, less compact, and exhibited more or less considerable evidence of vesicular structure.

---

* The term level is of course simply applied to the absence of a depression in the centre of the surface. All the ingots exhibited a more or less wrinkled upper surface.

It had been my intention to make a similarly extensive examination for oxygen, of ingots of refined copper from other well-authenticated localities, but it has been impossible for me to accomplish this up to the present time.

I have already referred to a specimen of copper which had been specially treated, with the object of purifying it completely from oxygen, and have briefly described the mode of treatment adopted for this purpose. The metal operated upon in this and other similar experiments was some of the Kapunda copper, of which the above examinations were instituted. The quantity of metal operated upon in different experiments varied between one and three pounds. All the specimens, of which the results of examination are given below, were allowed to cool down perfectly before the crucible was opened. The surfaces of these specimens were quite clean, highly crystalline, and exhibited very considerable depressions and cavities. The metal was in every case fibrous in character and exceedingly tough.

*Experiment* 1.—A portion of one of these specially prepared specimens was twice submitted to examination for oxygen; in neither instance was any indication obtained of the presence of that element in the specimen; in other words, the entire quantity of sulphuric acid employed in the process remained to be neutralised by the carbonate of soda.

*Experiment* 2.—A second specimen, similar to that used in Experiment 1, was examined; specimens being taken for this purpose from different parts of the metal. The following results were obtained:—

| No. of experiment. | Percentage of Oxygen. | Percentage of Suboxide of Copper. |
|---|---|---|
| 1 | 0·00 | 0·00 |
| 2 | 0·022 | 0·196 |
| 3 | 0·022 | 0·196 |
| 4 | 0·014 | 0·125 |
| 5 | 0·00 | 0·00 |
| 6 | 0·015 | 0·134 |

Determinations 1 and 5 were made with metal taken from the exterior of the sample; Nos. 3, 4 & 6, with specimens taken from the interior. The metal under examination had, therefore, not been uniformly freed from oxygen by the treatment which it had received.

*Experiment* 3.—A third specimen of copper, which had been submitted for a long-continued period to the treatment with charcoal, was examined. Two samples were taken from different parts of the interior of the specimen; in neither experiment was any indication of oxygen obtained.

*Experiment* 4.—A fourth sample, treated similarly to that used in Experiment 3, was also examined. Specimens taken both from the exterior and interior, furnished no indications of the presence of oxygen.

Some samples of Kapunda copper were operated upon in a manner precisely similar to that by which those above referred to were prepared; instead, however, of allowing the metal to cool down in the closed crucible, the lid of the latter was removed while the metal was still liquid. In those instances, just before the point of complete solidification, when the upper surface was already partially solid, a very considerable sprouting of the metal took place; in some instances a large very spongy excrescence of metal was formed upon the surface of the mass by the projected portion. The principal mass of the metal was highly vesicular in these instances, and contained oxygen.

The following results were obtained in the examination for oxygen of a series of specimens of copper in different conditions, from dry copper to over-poled copper, obtained from the Haford works of Messrs. Vivian, and for which I am indebted to the kindness of Mr. Morgan:

*Experiment* 1.—The sample of *over-poled* copper was first submitted to examination; the following four results were obtained with portions of the metal removed by consecutive treatment of one and the same piece of the sample with nitrate of silver:—

| | Percentage of | |
|---|---|---|
| | Oxygen. | Suboxide of Copper. |
| No. 1 | 0·025 | 0·223 |
| 2 | 0·026 | 0·232 |
| 3 | 0·030 | 0·268 |
| 4 | 0·040 | 0·357 |

The proportion of oxygen in the specimen was therefore slightly higher towards the centre of the ingot than in the exterior. A fifth determination made with a fresh sample taken from the centre of the specimen, furnished 0·035 per cent. of oxygen, or 0·312 per cent. of suboxide of copper.

*Experiment* 2.—A sample of *tough pitch* copper, the next in this series, furnished, upon examination of pieces taken from different parts of the specimen, the following results :—

1 .. 0·025 p. c. of oxygen, 0·223 p. c. of suboxide of copper.
2 .. 0·036 „ 0·321 „

*Experiment* 3.—Portions were dissolved off consecutively from a large fragment of a specimen of *half-poled* copper. They furnished the following results :—

1 .. 0·181 p. c. of oxygen, 1·616 p. c. of suboxide of copper.
2 .. 0·210 „ 1·873 „

A third determination was made in a fresh portion of this specimen, taken near the centre of the sample; the percentage of oxygen found was 0·198, equivalent to 1·766 per cent. of suboxide of copper.

*Experiment* 4.—The sample of *dry* copper of this series, contained one or two cavities coated with suboxide of copper. The specimens for analysis were taken from that part of the ingot which was apparently quite uniform in character. The following results were obtained :

| | Percentage of | |
|---|---|---|
| | Oxygen. | Suboxide of Copper. |
| 1 .. .. | 0·124 .. | 3·782 |
| 2 .. .. | 0·420 .. | 3·750 |

*Experiment* 5.—These results, though they corresponded very closely with those furnished by some specimens of dry copper which I had previously prepared, were so greatly below the numbers which Percy and Dick have published, as representing approximately the proportion of oxygen in a specimen of dry copper—also obtained from the Hafod works—that I was induced again to apply to Mr. Morgan for a specimen of the driest copper with which he could furnish me. That gentleman was so kind as to forward to me a second specimen, which he stated to be as dry as it ever was obtained in the course of working.

Two samples taken from the upper part of this ingot, furnished the following numbers:—

| | Percentage of— | |
|---|---|---|
| | Oxygen. | Suboxide of Copper. |
| 1 | 0·516 | 4·603 |
| 2 | 0·508 | 4·531 |

A sample from the bottom of this ingot contained 0·441 per cent. of oxygen, or 3·934 per cent. of suboxide of copper.

Several specimens of dry copper were prepared for examination by melting two or three pounds of metal in a capacious crucible, and exposing the liquid metal for long-continued periods to the air. The products thus obtained were quite similar in fracture and physical characters to the samples of dry copper received from Swansea. They were found to contain suboxide of copper, in quantities ranging, in the different specimens, from 3·5 to 3·8 per cent. Attempts were made to determine the maximum quantity of suboxide which copper was capable of dissolving, by gradually adding protoxide of copper to the melted metal; very considerable quantities were dissolved in this way, but no specimens sufficiently homogeneous in their character to furnish analytical results of any value could be obtained.

In reviewing the results described in the preceding pages as having been obtained with the method described for determining the proportion of oxygen in copper, I would wish, in the first instance, to record my opinion, that the data which they furnish regarding the proportions of oxygen which exist in refined copper, and in the metal at different stages of its treatment, though they are somewhat numerous and very definite, are not nearly of an extent or a variety sufficient to warrant the deduction from them of any positive conclusions respecting, 1st, the limits of the proportions of oxygen which exist in refined ingot copper, as sent into the market from different sources; or, 2nd, the extent to which the existence of that element (or of the suboxide of copper) in the metal, in its different stages, from dry to over-poled copper, may be likely to influence its properties, when it is pure or when it contains other foreign elements, in addition to oxygen.

Nevertheless, the high degree of confidence which I place in the general correctness of the results furnished by the method of estimating oxygen in copper which I have described, leads me to consider that they favour the following opinions:—

1. The proportion of oxygen which exists generally in the product known as dry copper, is probably much lower than has been hitherto believed by those authorities who have given their attention to this subject. The high results (10·21 and 9·34 per cent. of suboxide of copper) obtained by Dick in operating with hydrogen upon a sample of dry copper, obtained from the same source whence samples were procured by me (in which only 3·77 and 4·56 per cent. of suboxide of copper were found) appear to me ascribable, at any rate in part, to the very great uncertainty of that process of examination; and the method of estimating the proportion of oxygen in copper by determining the amount of pure metal in a given specimen, and taking the deficiency in the amount recovered as representing the oxygen, is certainly not more likely to have furnished an approximate result, since every tenth per cent. of impurity in the specimen of copper would thus be made to represent about three-quarters per cent. of suboxide of copper.

2. The circumstance, that a specimen of over-poled copper and one of tough pitch copper, both obtained from Hafod works, were found to contain essentially the same proportion of oxygen, was to me quite unexpected, and points to the necessity of a series of comparative experiments with tough pitch copper and the *same* metal in an over-poled condition, with the object of ascertaining the relative proportions of oxygen in them, in order that sufficient practical data may be obtained to test the soundness of the existing theory, that the difference in the properties of the metal in those two conditions may be due, either directly or indirectly, to the proportion of suboxide of copper present in each variety. I consider it right to state, however, that the results of experiments and observations, which unfortunately are of too fragmentary a nature to render their publication useful or even possible, lead me to doubt whether that view can be considered as fully or satisfactorily accounting for the results which attend the over-poling of copper. The observations of Percy and Dick, that a pure copper, so treated as to deprive it almost or entirely of oxygen, does not lose its toughness and other workable qualities, as ordinary tough pitch copper does, when over-poled, were fully confirmed by my experiments with pure "Kapunda" copper.

The comparatively large but variable quantities of oxygen found in the numerous ingots of *Kapunda* copper (which were intended for foundry purposes), and the very small proportion found in the specimen of *tough-pitch* copper, indicate a very considerable variation of the quantity of suboxide of copper existing in different varieties of the refined metal as sent into the market; and show, that an examination of the physical properties of different varieties of refined copper, combined with a determination of the proportions of oxygen and of the other impurities which they contain, would furnish data of interest and probably of considerable value. Those ingots of Kapunda copper used in the above experiments, which were richest in oxygen, were similar in their appearance and properties, to dry copper; they broke easily under the blow of a heavy hammer, and the attempts to forge a piece of one of these ingots cold, under a small steam hammer, were unsuccessful; the metal cracked in several places after two or three blows, and before it had suffered any important change of form. Those ingots of the same metal which contained the smallest proportions of oxygen (the upper surface of which were free or nearly so from central depressions or grooves), exhibited, as already described, a considerable difference from the above, in their fractures, and behaved also very differently when treated under the hammer. They were broken with greater difficulty, and a piece of such an ingot 1·75 inches deep, 2¼ inches long, and 1·75 inches thick, was hammered out under powerful blows to a square bar 3·9 inches long and 1·4 inches thick before it cracked. The specimens of copper (tough pitch, &c.) received from the Hafod works, were found as nearly as possible equal in purity to the Kapunda copper operated upon; it was therefore interesting and useful to compare their behaviour under the hammer with the above results. The half-poled copper (containing 1·731 per cent. of suboxide of copper) withstood a considerably larger number of blows without cracking, than the Kapunda copper which contained 2·595 per cent. of suboxide. The piece under treatment, after being elongated from 3 inches to 3·7 inches, broke at once through the centre. This specimen, therefore, though considerably more workable than the "Kapunda" which contained 0·866 per cent. *more* of suboxide of copper, was not nearly as tough as the Kapunda ingot, which contained 0·589 per cent. *less* of suboxide. The specimen of Hafod tough-pitch copper, containing 0·272 per cent. of suboxide of copper, exhibited, as might have been expected, considerably more toughness and malleability than the Kapunda specimen, which contained

0·87 per cent. more of suboxide. The ingot was broken with considerable difficulty, and a piece was hammered out from 3 inches to a square bar 4·7 inches in length, before it cracked. Thus far, then, the toughness and malleability of the Kapunda and Hafod copper were in inverse proportion to the quantity of suboxide of copper contained in the metal. Upon submitting, however, to treatment under the hammer, a piece of the *over-poled* copper from Hafod, which was quite as pure as the *tough-pitch* copper, and contained almost identically the same proportion of suboxide of copper (0·278), it was found to correspond in malleability to the Kapunda copper which contained 1·142 per cent. of suboxide of copper. To what is the great difference in the malleability of these specimens of tough-pitch and over-poled copper to be ascribed? The thorough analytical and physical examination of numerous specimens of copper, both in the tough and over-poled conditions, may furnish, and cannot fail to contribute to, a satisfactory solution of this problem.

## II.—*Carbon in Copper.*

The very interesting experiments described by Dick in the communication already referred to, which he instituted for the purpose of ascertaining whether and to what extent carbon is retained in combination by copper, when the metal has been exposed to modes of treatment most favourable to its union with that element, furnish evidence decidedly in favour of the conclusion that copper has no tendency to combine with, or at any rate to retain in combination, any appreciable proportion of carbon. From Dick's results, and from careful critical examination instituted by Percy in his metallurgic work, of those results, and of the statements made by Karsten, with regard to the combination of copper with carbon, and the influence exerted by that element upon the physical characters of the metal, it appears evident that the effects ascribed by the latter chemists to the union of copper with carbon are due to results, brought about, it is true, by the treatment which the metal receives with carbonaceous substances, but not traceable to the retention of any appreciable proportion of carbon by copper. The results of experiments instituted by me in this direction, some of which were already completed before the publication of Dick's paper, afford further support to the conclusion that Karsten was led, by the results of some analytical experiments, at any rate to over-estimate greatly the extent to which carbon entered into combination with copper.

The specimens of copper operated upon in the following experiments were specially prepared from some of the purest descriptions of refined copper (*i. e.* from selected samples of Alten and Kapunda copper). About three pounds of the copper were submitted to treatment with charcoal, for periods of one hour and upwards, according to the same method as that used for abstracting oxygen from copper. The products thus obtained possessed beautifully clean surfaces, exhibiting a highly crystalline appearance and considerable depressions. Upon breaking and cutting them, they were found to be exceedingly tough, and did not present any trace of vesicular structure. The following experiments were instituted with these specimens:

*Experiment* 1.—A piece of the perfectly clean copper, weighing 450 grains, was submitted to electrolysis. A very minute dark-coloured residue was obtained, which on careful examination, furnished no decided evidence of the presence of carbon.

*Experiment* 2.—A specimen, weighing 200 grains, was digested with very dilute nitric acid, until only a minute, almost black, residue remained. This appeared to contain a very minute quantity of carbon, but consisted almost entirely of chloride of silver.

*Experiment* 3.—310 grains were digested in a neutral solution of nitrate of silver, until the copper had been entirely converted into nitrate. The precipitated silver was amalgamated with pure mercury; a very small quantity of black matter was thus brought to light, which was separated by washing from the amalgam. It was examined for carbon, but the existence of that substance in it was only doubtful.

*Experiment* 4.—200 grains of a specimen of Alten copper were digested in an acidified solution of sesquichloride of iron, until all the metal had disappeared. The black residue found in the solution was too minute to be submitted to any examination.

*Experiment* 5.—A larger mass of the same specimen was digested for a lengthened period with the mixture of sesquichloride of iron and hydrochloric acid. On removing the remnant of copper from the liquid, 780 grains were found to have been dissolved. The liquid was allowed to stand in a covered vessel until a quantity of subchloride of copper which had been deposited, had passed into solution. A small black flocculent and extremely light residue was then observed at the bottom of the solution; this was carefully collected upon a plug of freshly-ignited asbestos, in a glass tube constricted at one end. After being thoroughly washed and dried, the asbestos-plug was placed upon platinum foil and introduced into a Bohemian glass tube, connected, at one extremity with an apparatus for delivering pure air, and, at the other, with accurately-weighed potassa-bulbs. When the asbestos-plug and the black residue were heated in a current of pure dry air, a sublimate was formed in the tube, of which more will be said. At the close of the experiment the potassa-bulbs had increased 0·146 grn. which would, if due entirely to carbonic acid furnished by the black flocculent matter, correspond to 0·0397 grains of carbon obtained from 780 grains of metal, or 0·005 per cent. It need scarcely be said that, in spite of extraordinary precautions adopted to exclude every source of error, the above slight increase upon the weight of the potassa-bulbs must be received with reserve as a positive indication of the existence of even so small a percentage as that named, in the sample of copper examined.

## III.—*Selenium in Copper.*

In the experiment No. 5, made with a specially-prepared specimen of Alten copper, with the view to ascertain whether any evidence of the existence of carbon in the specimen could be obtained; it was observed that, upon heating in a current of air the small black residue which had been obtained by treatment of the copper with an acidified solution of sesquichloride of iron, a sublimate was formed upon the glass tube, in close proximity to the plug of asbestos, upon which the residue had been collected.

This sublimate, in its thickest parts, was nearly black, the thinner portions presented a red-brown appearance. A small portion of it, when heated upon platinum in the open air, first fused to a lustrous blackish globule, and then burned with a blue flame, giving the characteristic odour afforded by selenium. The identity of the sublimate with selenium, was confirmed by the following results of its examination: it was insoluble in water; nitro-hydrochloric acid dissolved it, and the solution furnished a white precipitate with chloride of barium, and a reddish-brown precipitate of selenium when treated with sulphurous acid.

This accidental discovery of selenium in refined copper led to the examination of numerous specimens of copper from different countries for that element. The method of examination which was adopted, after its delicacy had been sufficiently established by test-experiments, was as follows :—1000 grains of the copper were dissolved in nitric acid; after removal of the principal excess of acid by evaporation, the solution was diluted; carbonate of soda was then added gradually until a small proportion of the copper was precipitated; this precipitate, which contained all the selenium present in the metal, was collected and dissolved in hydrochloric acid; the solution was boiled with sulphurous acid, when, if selenium was present, a brown or black precipitate was obtained; if of the latter colour, it contained selenide of copper. By dissolving this precipitate in nitric acid and reprecipitating with sulphurous acid, the selenium was obtained pure.

Several specimens of Alten copper were thus examined, and all were found to contain selenium, the largest quantity detected being only 0·003 per cent. A specimen of North American copper was found to contain a minute trace of this element, but none was detected in specimens of Copiapo, Manilla, Hungarian, and Italian copper, which were submitted to the method of examination described.

### IV. *Sulphur in Copper.*

Percy and Dick have pointed out that distinct evidence of sulphuretted hydrogen is obtained upon passing hydrogen over a heated specimen of copper containing a large proportion of suboxide of copper. In every one of very many instances in which I have submitted refined copper, containing both large and small proportions of suboxide, to treatment with pure hydrogen, I have obtained evidence of the formation of sulphuretted hydrogen. Although sulphur does not appear, from these results, to be ever completely abstracted from copper during the refining process, I have not met with any instance in which it existed in the metal in other than very minute proportions. But this minute proportion is obstinately retained by copper, when under treatment with hydrogen at a red heat. It was found necessary to pass the gas in one instance for more than forty-eight hours over the heated copper, in the state of filings, before the whole of the sulphur was eliminated. In this particular experiment, the pure gas was passed over 1000 grains of copper; the filings were confined in a Bohemian glass tube between plugs of asbestos, and were exposed to the highest temperature attainable in a gas-furnace. The gas passed from the tube through a solution of lead. After the treatment had been continued for forty-eight hours, the precipitate of sulphide of lead which had formed was collected and converted into sulphate. The sulphur which had been obtained from the copper in this experiment, amounted to 0·0045 per cent. On again exposing the same metal to treatment for some hours, a further minute proportion of sulphide of lead was formed, but the quantity was too small to be collected. In the second experiment, with a further quantity of the same copper, in which 0·0047 per cent. of sulphur was obtained, it was found that the principal proportion of that element was eliminated from the metal in four hours, but that minute quantities continued to pass off as sulphuretted hydrogen, long afterwards.

Numerous experiments have been instituted for the purpose of ascertaining whether the existence of *phosphorus* or *nitrogen* could be traced in refined copper. In searching for phosphorus, the following method was adopted, having first been accurately tested and proved to be sufficiently delicate for the detection of 0·02 per cent. of phosphorus in copper:

1000 grains of the metal were dissolved in nitric acid, the principal excess of the latter was expelled by evaporation, the solution was diluted, and carbonate of soda was then added until a small proportion of the copper was permanently precipitated. This precipitate, which would contain the whole of the phosphate of copper, was collected, suspended in water, and decomposed by hydrosulphuric acid. The filtrate from the sulphide was then examined in the ordinary way for phosphoric acid. Numerous specimens of refined copper have been examined by this method, but in none of them was any trace of phosphorus detected.

The experiments instituted with the view of searching for nitrogen in refined copper were less conclusive in their character, for the reason that the methods of treatment to which the metal was submitted were necessarily of a very protracted nature. They were consequently subject to unavoidable interruptions, and have not as yet been so thoroughly elaborated as to warrant me in making any positive statement regarding the freedom from nitrogen of the specimens operated upon. As far as they have been carried out, however, they have appeared to furnish results which, if not absolutely negative, did not point to the existence of nitrogen in any appreciable proportion, in the specimens examined. Two of the methods which it was attempted to apply to the detection of nitrogen may be briefly described. The one consisted in digesting small fragments of the copper in pure, moderately concentrated hydrochloric acid in an apparatus from which air was perfectly excluded, and eventually distilling the resulting solution with an excess of lime, the distillate being examined for ammonia. By the other method, the fragments of copper were introduced into a conical glass vessel with a delivery-tube accurately ground into the aperture. Suitable proportions of bichromate of potassa and sulphuric acid were added to the metal, and the vessel and delivery-tube were completely filled with freshly boiled water. The flask was then placed in a water-bath, and the mouth of the delivery-tube was covered by an inverted glass cup, filled with freshly-boiled water. In one experiment of this kind, carried on for several weeks, a very small quantity of gas had collected in the shoulder of the delivery-tube, which might have been either carbonic acid or nitrogen; but the quantity was too small to admit of being satisfactorily examined. It should be mentioned, that before the experiment was started, the vessel was entirely filled with solution of bichromate of potash and sulphuric acid, and was heated for some time, for the purpose of thoroughly cleaning the interior of the apparatus.

In dissolving specimens of refined copper by the various methods employed in the course of the experiments which have been described, minute quantities of dark insoluble matter were very frequently observed in the solutions. This residual matter was found to contain silicon and traces of iron, derived in all probability from minute particles of slag inclosed in the metal. It also generally contained small quantities of some substance, the nature of which has not yet been satisfactorily determined. It is scarcely probable that any appreciable quantity of silicon can be retained in actual combination by refined copper, but, owing to the above circumstance, no absolute information on this point can be furnished by the examination of specimens of copper for silicon.

Although the experiments, having reference to the existence and effects of oxygen in refined copper, were, for special reasons, instituted chiefly with one particular variety of that metal, the investigations for other non-metallic elements have been carried out with specimens of copper from a considerable variety of sources. I believe, therefore, that the results given in this communication may be considered to demonstrate that the only non-metallic elements, the existence of which in refined copper has, up to the present time, been conclusively established, are: *oxygen* and *sulphur*, as general constituents; the former in variable and sometimes considerable proportions, the latter only in minute quantities; and *selenium*, as an occasional constituent.

## XX.—*On the Hexyl-Group.*

By J. Alfred Wanklyn and E. Erlenmeyer.

### *β Iodide of Hexyl*, $\beta C_6H_{13}I$.

In the preparation of this substance from mannite, we now employ phosphorus to act upon the iodine which is liberated during the reaction, and by this means obtain as much as 90 per cent. of the theoretical quantity of the β iodide.* Moreover, this modification of the process enables us to make large quantities at once. The total amount of β iodide which we have prepared in different operations amounts altogether to more than 2 kilogrammes, from which it may be inferred that the operation has now become very easy.

As we have before mentioned, one of the most remarkable peculiarities presented by the β iodide is, that it readily splits up into hexylene and hydriodic acid, when it reacts upon alcoholic potash and upon various salts.

We have made an estimation of the amount of hexylene given by allowing an alcoholic solution of potash to act upon a known quantity of β iodide of hexyl. In one experiment

151·2 grm. of β iodide gave 44·4 grm. of $C_6H_{12}$.

The theoretical quantities, according to the equation

$$C_6H_{13}I = C_6H_{12} + HI$$

are:—

151·2 grm. of β iodide of hexyl, and 59·9 grm. of $C_6H_{12}$.

Thus the yield appears to be about 75 per cent. of the theoretical quantity; but it must not be forgotten that there are

---

[*] Chem. Soc. J. [2], i, 223 (1863).

sources of loss which are inseparable from a determination of this kind.

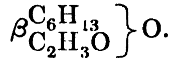
A little β hexylic alcohol seems always to be formed in the above reaction.

Among other re-agents which we have recently tried upon β iodide of hexyl, the sulphide and sulphydrate of potassium merit particular notice. Neither of these substances in alcoholic solution yields hexylene by reaction with our β iodide. In both cases the result is a sulphur-compound of hexyl. Very curious fact—the β alcohol tends to split into water and hexylene at the moment of formation—the β sulphhydrate or β sulphide does not show any tendency to this splitting.

### β. *Chloride of Hexyl*, β $C_6H_{13}Cl$.

This compound may be prepared by saturating the β alcohol with dry hydrochloric acid, sealing up in a glass tube and heating to about 100° C. After a time, two layers of liquid appear in the tube, the upper layer being the chloride and the lower an aqueous solution of hydrochloric acid. This aqueous solution must be removed, dry hydrochloric acid again led into the organic liquid, and the sealing and heating repeated. No hexylene results. β chloride of hexyl is a liquid, boiling point between 120° and 130° C. With alcoholic solution of potash it gives hexylene. We intend to study it further. A combustion of it with chromate of lead gave 61·08 % of carbon and 11·73 % of hydrogen: the formula of chloride of hexyl requiring 59·75 % of carbon and 10·79 % of hydrogen. The discrepancy is obviously due to the presence of some undecomposed β hexyl-alcohol.

### β *Acetate of Hexyl*



$\beta\left.\begin{matrix}C_6H_{13}\\C_2H_3O\end{matrix}\right\}O.$

It has been previously mentioned that we failed to get the acetate by using acetate of lead and β iodide of hexyl, obtaining hexylene instead. With acetate of silver we had no better success. In both instances the main product was hexylene, all the indications of acetate of hexyl that we could obtain being limited to a peculiar smell (since ascertained to be the smell of the body in question), but no tangible quantity of any other organic product except hexylene being obtained.

For the preparation of the acetate we were forced to resort to other reactions. We made β hexyl-sulphuric acid (from hexylene and sulphuric acid of the proper strength) and diluted it with many times its volume of glacial acetic acid (1 vol. to 8 or 10 vols. of glacial acetic acid answers very well) and distilled. The distillate, after being well washed and dried, is β acetate of hexyl. The following equation explains its formation :—

$$\beta\left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 + \beta\left.\begin{matrix}C_2H_3O\\C_6H_{13}\end{matrix}\right\}O$$

Combustions of the acetate have been made.

| | Calculated. | | Found. I. | Found. II. | Found. III. |
|---|---|---|---|---|---|
| $C_8$ | 96 | 66·67 | 66·56 | 67·10 | 67·14 |
| $H_{16}$ | 16 | 11·11 | 11·18 | 11·49 | — |
| $O_2$ | 32 | 22·22 | — | — | — |
| | 144 | 100·00 | | | |

Boiling-point 155° to 157° C. (corrected) under a pressure of 787 millimetres.

Sp. gr. at 0° C. = ·8778
" 50° C. = ·8310

Therefore the expansion-coefficient for 50° C. = ·0563.

It is insoluble in water, and does not smell like the acetates of the alcohol-radicles usually do. It is a remarkably stable compound, being capable of bearing a heat of 200° C. for twelve hours without undergoing any alteration. Analysis I. was made upon a portion which had been sealed up and exposed for twelve hours to a temperature ranging from 200° to 220° C.; it had not the slightest acid reaction, and distilled in the same manner as before heating.

An alcoholic solution of potash decomposes the β acetate at 100° C., but gives no hexylene. The products are acetate of potash and β hexylic alcohol.

*β Hexyl-alcoholate of Sodium.*—β $C_6H_{13}NaO$ (formed by acting upon the β alcohol with sodium), forms, with β acetate of hexyl, a double compound which the addition of water transforms into β hexyl-alcohol and acetate of soda. Neither hexylene nor β hexyl-ether could be detected.

### *β Hexyl-mercaptan* $\beta \left.\begin{matrix} C_6H_{13} \\ H \end{matrix}\right\} S$

As above indicated, this compound is the sole organic product of the action of sulphhydrate of potassium dissolved in alcohol upon β iodide of hexyl. The reaction takes place very readily, yielding the theoretical quantity of β hexyl-mercaptan, which has of course a bad smell.

β hexyl-mercaptan combines with oxide of mercury with great energy. It boils at about 142° C. (corrected), barometer = 760 millimetres. Its boiling-point is therefore about that which *a* hexyl-mercaptan should have. Sp. gr. at 0°C. = 0·8856. It is nearly insoluble in water. It is, however, sufficiently abnormal. It combines with solid potash, and energetically even with aqueous solution of potash, giving a homogeneous liquid when shaken up with a strong aqueous solution of that alkali, and generating considerable heat. This compound with potash possesses the extraordinary property of being decomposed at 100° C. We extract the following from our note-book :—" 1 vol. of β hexyl-mercaptan shaken up in a sealed tube with 4 vols. of aqueous potash, sp. gr. 1·22 ; tube becomes warm, by-and-by only one layer of liquid in the tube. Heated to 100° C.; turbidity and then two distinct layers ; let cool, shake up ; only one layer in tube."

We are engaged with the further study of this most interesting body. It has been analyzed.

·1900 grm. burnt with chromate of lead and a little bichromate of potash gave ·4284 grm.; $CO_2$ and ·2120 grm. $H_2O$.

| | Calculated. | | Found. |
|---|---|---|---|
| $C_6$ | 72 | 61·02 | 61·56 |
| $H_{14}$ | 14 | 11·86 | 12·40 |
| S | 32 | 27·12 | — |
| | 118 | 100·00 | |

Sodium acts upon it, evolving hydrogen and forming a white solid, which is, no doubt, the β hexyl-mercaptide of sodium.

β Hexyl-mercaptide of mercury Hg $\left\{\begin{matrix} \beta C_6H_{13}S \\ \beta C_6H_{13}S \end{matrix}\right.$ is liquid even at 0°C. It is insoluble in water and in alcohol, but dissolves readily in ether. Sp. gr. at 0°C. = 1·6502.

# XXI.—*On Oxaniline.*

By Dr. R. Schmidt, Assistant at the Chemical Institute of Marburg.

[Communicated by Prof. Kolbe.]

## Preliminary Notice.

Nitrosalicylic acid is easily converted, by treatment with tin and hydrochloric acid, into amidosalicylic acid, a compound which crystallizes in splendid needles, and like most other amido-acids forms salts both with bases and with the stronger acids.

One of the numerous products of the decomposition of amidosalicylic acid which I have investigated, is oxaniline. This body is produced quite simply by the destructive distillation of amidosalicylic acid; and if the acid to be heated is previously mixed with twice its weight of powdered pumice, a tolerably abundant product will be obtained. The decomposition is represented by the equation:

$$\underbrace{HO.\left(C_{12}\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}O_2\right)\left[C_2O_2\right]O}_{\text{Amidosalicylic acid.}} = \underbrace{\left.\begin{matrix}C_{12}H_5O_2\\H_2\end{matrix}\right\}N}_{\text{Oxaniline.}} + C_2O_4$$

The sublimate obtained consists, partly of white needles, partly of a fused brown crust, smelling of ammonia and phenic acid. These secondary products are easily removed by treating the sublimate with alcohol slightly acidulated with acetic acid, the oxaniline then remaining as a white scentless mass.

Oxaniline is soluble in hot water and hot alcohol, and separates on cooling in wedge-shaped crystals, mostly somewhat coloured. The hot aqueous solution likewise turns brown when exposed to the air, and deposits a brown amorphous substance.

Oxaniline in aqueous solution very easily reduces the solutions of the noble metals, assuming at the same time a splendid violet colour. The same colouring is produced by nitric acid, when a few drops of it are added to the aqueous solution of the oxyaniline.

A very characteristic reaction of oxaniline is the fine deep indigo colour which its aqueous solution acquires by mixture with an alkaline liquid: this colour disappears, however, on addition of an acid.

Oxaniline unites very easily with chlorhydric, bromhydric, iodhydric, sulphuric, and other acids, forming soluble salts which crytallise with great beauty. The perfectly neutral solutions of these salts undergo a gradual alteration when exposed to the air; but in acid solution the salts are permanent.

I am still engaged with the further investigation of this interesting base, particularly with the view of exactly determining its relations to aniline.

## XXII.—*Note on an Alkaloïd contained in the Seeds of* the Ricinus communis, or *Castor-oil Plant.*

By Richard V. Tuson, F.C.S., Professor of Chemistry in the Royal Veterinary College.

It is well known that certain parts of several plants belonging to the natural order *Euphorbiaceæ*, as well as various pharmaceutical preparations obtained therefrom, have been long employed in medicine; and that, notwithstanding this circumstance, we are still but most imperfectly acquainted with the chemical constitution and physiological actions of the proximate principles upon which depend the therapeutic powers of such bodies. With the view of endeavouring to contribute information upon this subject, I have devoted much of the spare time which I could snatch from that devoted to my ordinary professional pursuits, to the isolation, if possible, of the active constituents of castor and croton seeds, and of the oils expressed from them, of gum-euphorbium and of cascarilla bark, *i. e.* the bark of *Croton cascarilla* or *Croton eleuteria.* Now although my essays in this particular direction have not at present been crowned with success, I have nevertheless discovered several substances in Euphorbiaceous plants which possess more or less chemical interest, and an account of which I hope shortly to publish. On some future occasion I intend furnishing the Society with a complete description of these bodies; but I take the present opportunity of partially describing an alkaloïd provisionally named ricinine, which I have discovered in the seeds of the ***Ricinus communis*** or castor-oil plant.

*Preparation of Ricinine.*—Crushed castor-seeds are boiled with, and exhausted by, successive quantities of water. The aqueous solutions thus obtained, after being passed through a wet calico filter to remove as much oil as possible, are evaporated over a water-bath to the consistence of an extract. This extract is exhausted by boiling alcohol, and the spirituous solution thus produced is filtered while hot. The filtrate on cooling deposits a small amount of resinoïd matters, which are separated by filtration. The filtered liquid is then deprived of its excess of alcohol by distillation, and allowed to stand all night. The next morning an almost white crystalline substance is found adhering to the sides and bottom of the vessel containing the above-named concentrated spirituous solution. This crystalline body is ricinine, and in order to obtain it in a pure state it is only necessary to crystallize it from alcohol several times, and decolorize it with animal charcoal.

*Properties of Ricinine.*—Ricinine crystallizes in rectangular prisms and plates. When placed on the tongue it slowly manifests a feebly bitter taste, somewhat resembling that of bitter almonds. Cautiously heated on a glass plate, it melts and forms a colourless and mobile liquid, which, on cooling, solidifies into a whorl of acicular crystals. On heating it between two watch-glasses, a sublimate is obtained which appears to be unaltered ricinine. Strongly heated on platinum-foil, the alkaloïd first melts, and subsequently burns with a highly luminous and fuliginous flame.

Ricinine is pretty readily dissolved by water and by alcohol, but is only slightly soluble in ether and in benzol.

When ricinine is heated with solid hydrate of potassium, ammonia is evolved, proving that the alkaloïd contains nitrogen.

Concentrated sulphuric acid dissolves ricinine without colouring it, and the addition of bichromate of potassium to the solution simply causes the development of a greenish hue.

Iodic acid appears to undergo no change when brought in contact with ricinine, even though the mixture be warmed.

Both hot and cold concentrated nitric acid dissolve ricinine without evolving red vapours; and on evaporating the solution thus produced to a small bulk and allowing it to cool, groups of transparent and colourless acicular crystals form. These crystals are rendered opaque by the addition of water.

Concentrated hydrochloric acid dissolves ricinine, and the hydrochlorate of the base, which is doubtless produced in this reaction, appears to be easily decomposed, both by evaporation and by dilution. A solution of ricinine in concentrated hydrochloric acid does not give a precipitate with a concentrated aqueous solution of bichloride of platinum, but if a mixture of these compounds be evaporated more or less, well defined orange octahedrons of the chloroplatinate of ricinine crystallize out.

On mixing together cold saturated solutions of ricinine and mercuric chloride no change is at first observed; but if the mixture be allowed to stand for a few minutes, a mass of beautiful silky crystals, arranged in fasciculi, forms, which is so solid that the vessel in which the experiment is performed may be inverted without any fear of its contents falling out. This mercurial compound of ricinine is purified by crystallization from water or alcohol.

If ordinary castor-oil be shaken up with water, and the water afterwards separated from the oil, and evaporated to dryness over a water-bath, a small quantity of a resinous residue is left, which, when digested with boiling benzol, partly dissolves; and if this benzolic solution be allowed to evaporate spontaneously, crystals are obtained which, so far as one can judge from their physical qualities, consist of ricinine.

Neither ricinine nor the risinoïd body which falls when the alcoholic solution of the aqueous extract is allowed to cool, constitutes the purgative principle of castor-seeds; for I gave two grains of each of these substances (which are equivalent to several pounds of seed) to a rabbit about a month ago, and the animal has not evinced the slightest inconvenience.

By a process precisely similar to that which was employed in the isolation of ricinine, I have obtained an alkaloïd analogous to, possibly identical with, that base, from croton-seeds and oil.

It may be interesting and important to mention that Brandes, many years ago, announced the existence of an alkaloïd named cascarelline, in cascarilla bark, *i. e.*, the bark of *Croton eleuteria*, or *Croton cascarilla*, both belonging to the natural order *Euphorbiaceæ*. This alkaloïd, if we may judge from the published account of its properties, possesses similar physical qualities to those of ricinine, but the action of sulphuric and hydrochloric acids on the two alkaloïds is very different.

## XXIII.—*On the Tetrabasic or Orthocarbonate of Ethyl.*

### By Henry Bassett, F.C.S.

In the early part of last year, I published in the Chemical News,* a short note of some experiments on the subformate of ethyl, described by Williamson and Kay,† in which I gave a modified process by which it may be prepared in large quantity, namely, by adding sodium to a mixture of chloroform and absolute alcohol. Since then I have observed that, by adding an alcoholic solution of ethylate of sodium to chloroform, an evolution of very large quantities of gas takes place, consisting almost entirely of carbonic oxide, and the quantity of subformate of ethyl produced is very much smaller. This appears to be caused by the decomposition of some of the subformate by the ethylate of sodium, whereas, by adding the sodium to the mixture of alcohol and chloroform, there is always an excess of the latter, whereby this decomposition and consequent loss is prevented.

The secondary reaction may be represented as follows:

$$2\left.\begin{matrix}CH'''\\(C_2H_5)_3\end{matrix}\right\}O_3 + \left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O = CO + CHNaO_2 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + 3\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$$

Subform ethyl

and in reference to this equation, I may observe that it explains the formation of ether and alcohol, which was noticed by Williamson when using dry ethylate of sodium. The formate is readily detected by the usual tests in the watery solution of the residue left after distilling off the alcohol.

After absorption of the carbonic oxide by subchloride of copper, a small quantity of inflammable gas remains, and this is probably ethylene, as Hermann, who has analysed the gas produced by the action of alcoholic potash on bromoform, states‡ it to consist of carbonic oxide, with a trace of ethylene, which he considers to be formed catalytically.

During these experiments, the idea naturally suggested itself of examining the action of ethylate of sodium on some other chlorides, more or less allied to chloroform, but unfortunately, the Co

hydrochl

reaction, ap

---

ol. vii, p. 158.

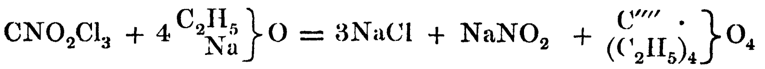
† Proceed. Roy. Soc. June, 1854.

‡ Ann. Ch. Pharm., xcv. 211.

chlorinated derivatives of chloride of ethyl, and the various chlorides of carbon, are either not attacked at all, or very slightly so, by ethylate of sodium, at all events below the temperature at which the ethylate alone would undergo decomposition. By the employment, however, of chloropicrin, which is attacked with great facility, I have succeeded in obtaining a compound, the composition, properties, and decompositions of which show that it must be regarded as a tetrabasic carbonate of ethyl.

The details of the process are as follows:

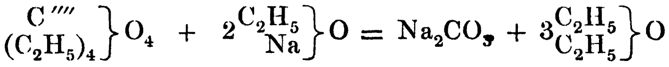
40 grms. chloropicrin are mixed with 10 oz. absolute alcohol in a flask adapted to an upright condenser. The flask is supported on a water-bath, and the temperature raised to the boiling point of the alcohol. 24 grms. sodium are then gradually added in portions of about half a gramme, the temperature being kept up during the whole time, as the reaction is not so easily effected as with chloroform. The alcohol is then distilled off in the water-bath, and the residue dissolved in water, when an oil floats on the top. The reaction is represented below:



$$CNO_2Cl_3 + 4\left.\begin{matrix}C_2H_5\\ Na\end{matrix}\right\}O = 3NaCl + NaNO_2 + \left.\begin{matrix}C''''\\ (C_2H_5)_4\end{matrix}\right\}O_4$$

Ortho-carb. ethyl.

Besides chloride and nitrite, the watery solution contains some carbonate of sodium, arising doubtless from a secondary decomposition of some of the oily product:



$$\left.\begin{matrix}C''''\\ (C_2H_5)_4\end{matrix}\right\}O_4 + 2\left.\begin{matrix}C_2H_5\\ Na\end{matrix}\right\}O = Na_2CO_3 + 3\left.\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right\}O$$

The smell of ether is distinctly perceptible in the first portions of the alcoholic distillate.

The hydrogen evolved during the process is alkaline, from the presence of ammonia derived from reduction of the chloropicrin. By passing it into dilute hydrochloric acid, a solution was obtained, which, on addition of bichloride of platinum, gave a salt, the analysis of which gave the following result:

·5195 grm. gave ·229 grm. platinum, corresponding to 44·08 p. c.
The ammonio-chloride of platinum contains . . . . 44·17 p. c.

The oil separated from the watery solution is washed, dried with chloride of calcium, and purified by fractional distill
By this means the pure substance is obtained as a col

of sp. gr. ·925, boiling at 158°—159°, having a peculiar aromatic smell, and giving the following results on analysis:

1. ·2835 grm. gave ·584 grm. carbonic acid and ·2665 grm. water.
2. ·2853 grm. gave ·586 grm. carbonic acid and ·269 grm. water.

These numbers agree closely with theory, as will be seen by comparison of the percentage amounts.

| | I. | II. | $\left.\begin{matrix}C''''\\(C_2H_5)_4\end{matrix}\right\}O_4$ |
|---|---|---|---|
| Carbon .......... | 56·18 | 56·02 | 56·25 |
| Hydrogen........ | 10·44 | 10·48 | 10·41 |

The substance, being rather difficult of combustion, required the employment of tubes rather longer than usual: granular oxide of copper was used, and oxygen passed through at the end of the process.

A determination of the vapour-density gave the following result:—

| | |
|---|---|
| Difference in weights of flask .... | ·519 grm. |
| Temperature of air............ .. | 10°·5 |
| Temperature of vapour .......... | 204° |
| Residual air........ .......... | 3·25 c.c. |
| Capacity of flask .. .......... | 141·5 c.c. |

The vapour-density calculated from these data is 6·80

That required by the formula $\left.\begin{matrix}C''''\\(C_2H_5)_4\end{matrix}\right\}O_4$ is 6·65

A small piece of sodium was ignited in the vapour, and the result carefully tested for nitrogen and chlorine; but not a trace of either was found.

On boiling a small quantity of the substance with alcoholic potash, a considerable quantity of carbonate was deposited.

10 grammes of the oil were digested at 100° for about six hours with 8 grammes boric anhydride, and the resulting solution distilled to dryness. The distillate was washed with dilute potash, and afterwards with water, to separate traces of boric ether carried over, dried with chloride of calcium, and then purified by distillation. Nearly the whole came over between 124°—126°, the boiling point of ordinary carbonic ether being 125°.

hydroch identity of the two substances is confirmed by the following reaction, ap

·3215 grm. gave ·596 grm. ca onic acid and ·247 grm. water, leading to the percentage amount :—

| | Experiment. | $(C_2H_5)_2CO_3$. |
|---|---|---|
| Carbon ......... | 50·56 | 50·85 |
| Hydrogen ...... | 8·54 | 8·47 |

The reaction may be represented as follows :—

$$\left.\begin{matrix}C''''\\(C_2H_5)_4\end{matrix}\right\}O_4 + 2B_2O_3 = \underset{\text{Biborate ethyl.}}{(C_2H_5)_2B_4O_7} + (C_2H_5)_2CO_3,$$

which is similar to what takes place with the subformate of ethyl, ordinary formic ether being in that case produced.

From the foregoing results there can, I think, be no doubt that the substance in question is really a tetrabasic carbonate of ethyl; and the discovery of analogous ethers may be not unreasonably expected.

The next homologue to Williamson's tribasic formate of ethyl, the tribasic acetate, would in all probability be formed by the action of ethylate of sodium on Malaguti's bichlorinated ether, in the following manner :—

$$\underset{\text{Bichlor. Ether.}}{\left.\begin{matrix}C_2H_3{}'''\\C_2H_3{}'''\end{matrix}\right\}\begin{matrix}O\\Cl_4\end{matrix}} + 4\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O = 4NaCl + \underset{\text{Acet. Ether.}}{\left.\begin{matrix}C_2H_3{}'''\\C_2H_5\end{matrix}\right\}O_2} + \underset{\text{Tribasic Acet. Ether.}}{\left.\begin{matrix}C_2H_3{}'''\\(C_2H_5)_3\end{matrix}\right\}O_3}$$

In connexion with this may be mentioned the well-known fact, that the density of glacial acetic acid is increased up to a certain point by the addition of water; and this apparent anomaly would seem to show a tendency to form a hydrate of analogous constitution, as the acid at its greatest density has the composition being $C_2H_4O_2.H_2O$, which might then be written $\left.\begin{matrix}C_2H_3{}'''\\H_3\end{matrix}\right\}O_3$. Vale-

It lic acid is said to be invariably obtained in the form of a other ate of analogous composition, when a solution of a valerianate the typomposed by an acid.

value. e ordinary and the tribasic formic ethers stand in a very were cesting relation to the glycerides and the glycidic ethers I haibed by Reboul :*

---

* Ann. Chim. Phys. [3], lx, 1.

$$\left.\begin{array}{l} CH''' \\ C_2H_5 \end{array}\right\} O_2$$

Formic ether.

$$\left.\begin{array}{l} CH''' \\ (C_2H_5)_3 \end{array}\right\} O_3$$

Ortho-formic ether.

$$\left.\begin{array}{l} C_3H_5''' \\ C_2H_5 \end{array}\right\} O_2$$

Glycidic ether.

$$\left.\begin{array}{l} C_3H_5''' \\ (C_2H_5)_3 \end{array}\right\} O_3$$

Tri-ethylin.

The existence of two distinct series of isomeric bodies thus becomes probable, one derived from the triatomic alcohols, and the other from the fatty acids; and it would be interesting to ascertain whether the action of boric anhydride would produce the glycidic ethers directly from the glycerides.

In conclusion, I may make a few remarks suggested by the composition of the best defined basic salts of some of the acids derived from alcohols. These may be divided into two classes, namely, those whose normal basicity is less than their atomicity, and those in which it is the same. The most basic salts formed by the first class of acids appear to contain a number of atoms of metal equal to the number of atoms of water from which the original alcohol is derived. As examples may be mentioned, the bibasic lactates, the basic malates of copper and zinc, which contain three atoms of metal, some basic tartrates and citrates of copper containing four atoms, and a basic saccharate of lead containing six atoms of metal.

In the most basic salts of the second class, the number of atoms of metal exceeds the number of atoms of water from which the original alcohol is derived, and coincides with the atomic value of the alcohol-radicle, as altered by the removal of hydrogen. As examples may be given, the best-defined basic lead and copper salts of the fatty acids, which are similar in composition to the tribasic or ortho-formate of ethyl, the metallic orthocarbonates, also corresponding to the tetrabasic or orthocarbonate of ethyl, and several basic oxalates and succinates containing six atoms metal, ethers corresponding to which yet remain to be discove

# XXIV.—*On the action of Hydrobromic Acid and of Hydriodic Acid upon Polyatomic Acids, and on the behaviour of the Iodo-substitution compounds towards Hydriodic Acid.*

By Aug. Kekulé.

Formerly in considering organic acids, importance was attached only to their basicity; but latterly, and I believe I was the first who drew the attention of chemists to this subject, besides their basicity, their atomicity has also been taken into consideration. Three kinds of hydrogen are therefore distinguished in organic acids, according to the part it plays: 1st. Hydrogen which belongs to the radicle, according to the expression of the theory of types.

2nd. Typical Hydrogen. The latter is either easily substituted by metals (hydrogen of acids), or it does not possess this property (hydrogen of alcohols). Those polyatomic acids, whose basicity is less than their atomicity, stand, as regards the nature of the typical atoms of hydrogen, between the alcohols and those organic acids whose basicity is equal to their atomicity.

The cause of the difference between the typical hydrogen-atoms must be sought in the nature of those atoms which surround the respective hydrogen-atoms. It is, in fact, very apparent that the chemical nature of the place which these hydrogen-atoms occupy, must be the resultant of all the forces of attraction which the various atoms surrounding this place exercise.

According to the theoretical views which I formerly published, that hydrogen which, according to the theory of types, belongs to the radicle, stands in direct relation to the carbon-atom; the typical hydrogen is, on the contrary, in combination with the carbon-group, only through the mediation of oxygen. This typical hydrogen is easily substituted by metals, if there happens to be in its neighbourhood an atom of oxygen which is completely combined with carbon; if this is not the case, it has the behaviour of the typical hydrogen of the alcohols.

It will, therefore, be easily understood why, in glycollic and other polyatomic acids, whose basicity is less than their atomicity, the typical atoms of hydrogen are not absolutely of the same value. Such substances behave as though one side of the molecule were composed of an alcohol, and the other of an acid.

I have elsewhere explicitly shown that all known facts relating to this class of acids admit of, a simple explanation by this theory, and several chemists have since brought forward numerous observations, which, however, tend further to support it. But as the typical, but not acid, hydrogen-atoms of these acids are thus confounded by some chemists with the typical hydrogen-atoms of the alcohols, it appears to me to be appropriate to support my views by other facts.

It is now well-known that one of the most characteristic differences between alcohols and acids, is the facts that alcohols produce bromides or chlorides when acted upon by hydrochloric or hydrobromic acid,

$$C_2H_6O + HBr = H_2O + C_2H_5Br;$$

whereas with acids the same reaction takes place in precisely an inverted sense, so that the chloride or bromide undergoes decomposition by water; for example:

$$C_2H_3OBr + H_2O = HBr + C_2H_4O_2.$$

If now in glycollic acid and lactic acid, one side of the molecule behaves like an alcohol, these acids ought to exhibit the same behaviour as the alcohols with hydrobromic acid; they ought therefore to form the corresponding bromide by losing water. These bromides are well known to be identical with the products of substitution by bromine in acetic acid and propionic acid. The same bodies which, until now, have been obtained as products of substitution from acetic acid or propionic acid, ought therefore to be producible as ethers from glycollic and lactic acids.

Glycollic acid: $C_2H_4O_3 + HBr = H_2O + C_2H_3BrO_2$
Lactic acid: $C_3H_6O_3 + HBr = H_2O + C_3H_5BrO_2$.

In the same manner the formation of monobromosuccinic acid was to be expected from the dibasic and triatomic malic acid:

Malic acid $C_4H_6O_5 + HBr = H_2O + \underset{\text{Bromosuccinic acid.}}{C_4H_5BrO_4}$.

In a similar manner, dibromosuccinic acid might have been formed from the dibasic and tetratomic tartaric acid containing two alcoholic hydrogen-atoms:

$$C_4H_6O_6 - 2HBr = 2H_2O + C_4H_4Br_2O_4.$$

The experiments which I have made up to the present time have confirmed this opinion for all those acids which contain only one atom of alcoholic hydrogen.

*Glycollic Acid.*—When glycollic acid (formed by oxidation of alcohol) is heated to 100° with a cold concentrated aqueous solution of chemically pure hydrobromic acid, monobromacetic acid is produced. The monobromacetic acid thus obtained, boils at 205° to 208°, and congeals in the condensing tube to a crystalline mass. By treating it with sodium-amalgam, it could be transformed into acetic acid; by boiling with lime and water, it regenerated glycollic acid; by acting upon it with an alcoholic solution of ammonia, glycocoll was easily produced.

*Lactic Acid.*—Under the same conditions, lactic acid forms bromopropionic acid. This acid boils at 202° (corrected 205°·5), and congeals in a freezing mixture (17°) to a laminar crystalline mass. It forms propionic acid when treated with sodium-amalgam; when boiled with oxide of zinc, it yields lactate of zinc containing the same amount of water as the zinc-salt of ordinary lactic acid; when it is heated with an alcoholic solution of ammonia, alanine is readily formed.

*Malic Acid.*—This acid exhibits the same behaviour. On heating it to 100° with fuming hydrobromic acid for some hours, a considerable quantity of monobromosuccinic acid is formed. The acid thus produced appears to me to be identical with the monobromosuccinic acid which I formerly produced by acting upon succinic acid with bromine; I cannot, however, decide this question with absolute certainty. It forms small crystals, easily soluble in water, alcohol, and ether (1 part in 5·2 parts of water of 15°·5). It melts at 159°—160°, and is slowly decomposed even at this temperature, more quickly when heated more strongly, forming fumaric and hydrobromic acids. Bromosuccinic acid is therefore decomposed in a manner exactly similar to malic acid, of which it may be regarded as a hydrobromic ether:

$$C_4H_6O_5 = H_2O + C_4H_4O_4$$

Malic acid. Fumaric acid.

$$C_4H_5BrO_4 = HBr + C_4H_4O_4$$

Monobromosuccinic acid. Fumaric acid.

Monobromosuccinic acid when acted upon by sodium-amalgam easily yields succinic acid, which appears to be perfectly identical with ordinary succinic acid. It is decomposed with extraordinary facility by oxide of silver. The malic acid thus obtained is optically inactive, and appears to be identical with the inactive malic acid obtained from inactive aspartic acid. When monobromosuccinic acid is heated with an aqueous or alcoholic solution of ammonia, various amides are formed, one of which appears to be aspartic acid. From the facts here enumerated, we may conclude, with tolerable probability, that other polyatomic acids, containing only *one* atom of alcoholic hydrogen, will show the same behaviour.

For those polyatomic acids which contain *two* atoms of alcoholic hydrogen, the behaviour appears to be different. I have at least not been able to produce dibromosuccinic acid from tartaric acid; I obtained rather a comparatively small quantity of monobromosuccinic acid. Racemic acid exhibits precisely the same deportment. I shall, upon some future occasion, again refer to this formation of monobromosuccinic acid, and will here only mention that it is perfectly analogous to the formation of monoiodopropionic acid from glyceric acid.

I have hitherto studied the above-mentioned reaction, chiefly with hydrobromic acid, but I have proved qualitatively that hydrochloric acid shows a perfectly analogous behaviour. It might, therefore, be concluded that hydriodic acid would produce the same reaction; and if no substitution-products of acids containing less oxygen, are formed thereby, the cause of this negative result must be sought in a peculiar behaviour of iodo-substitution-compounds, of which I am now going to treat.

### *On the Action of Hydriodic Acid upon Iodo-Substitution-Compounds.*

Iodine, though generally speaking very similar in its behaviour to chlorine and bromine, shows, nevertheless, some differences worthy of remark. In general it acts much less energetically, and it never produces substitution-compounds, when acting, for example, upon organic substances. Many compounds of iodine have, on the contrary, the property of being easily decomposed, with liberation of iodine.

This difference between iodine on the one hand, and chlorine and bromine on the other, shows itself even in the simplest compounds, in its combination with hydrogen, for example.

Chlorine combines easily with hydrogen, and forms hydrochloric acid; hydriodic acid is, on the contrary, easily decomposed into iodine and hydrogen. Both reactions may be expressed by the same equation, but the decomposition takes place with chlorine in one sense, with iodine in the other.

For iodine we have:

$$HI + HI = H_2 + I_2$$

for chlorine:

$$Cl_2 + H_2 = HCl + HCl.$$

From a theoretical point of view, it appeared probable that this peculiarity of iodine might be found in all its compounds, and that, in many cases, in which chlorine produces a definite reaction, a precisely contrary reaction would be produced by iodine.

I presumed, amongst other things, that iodo-substitution-compounds would be decomposed by the action of hydriodic acid, so as to form the normal substances, with liberation of iodine, by an inverse substitution process.

The experiments hitherto made, have confirmed my expectation. I shall for the present confine myself to mentioning the results which I have obtained with iodo-substitution-compounds corresponding to organic acids.

When iodacetic acid (prepared according to the method of Perkin and Duppa) is brought into contact with a concentrated aqueous solution of hydriodic acid, reaction takes place, even in the cold, iodine being liberated and acetic acid formed.

The iodo-propionic acid, prepared according to Beilstein's method, by the action of iodide of phosphorus ($P_2I_4$), on glyceric acid, is likewise acted upon by hydriodic acid, but the action does not take place till about 180°, at which temperature propionic acid is formed. Both decompositions may be explained by the following equations:

$$\underset{\substack{\text{Iodacetic}\\\text{acid.}}}{\text{Ȼ}_2H_3I\Theta_2} + HI = \text{Ȼ}_2H_4\Theta_2 + I_2$$

$$\underset{\substack{\text{Iodopropionic}\\\text{acid.}}}{\text{Ȼ}_3H_5I\Theta_2} + HI = \text{Ȼ}_3H_6\Theta_2 + I_2$$

If this action of hydriodic acid on the iodo-substitution-compounds of organic acids proves to be of a general character, as from theoretical reasons I believe it to be, it becomes evident that iodo-substitution-compounds can never be formed by the direct action of iodine upon organic acids.

Now since, according to experiments made by Kolbe and Lautemann, and afterwards followed up by Lautemann alone, iodosalicylic acid is directly obtained by heating salicylic acid with iodine, it appeared to me to be of special interest to expose the iodosalicylic acid thus obtained to the action of hydriodic acid.

I have found that the mono-iodosalicylic acid produced by Lautemann's method, is easily attacked by hydriodic acid. The action takes place even below 100°, iodine being liberated, and salicylic acid formed, according to the equation:

$$\underset{\text{Iodosalicylic acid.}}{\mathrm{C}_7\mathrm{H}_5\mathrm{IO}^3} + \mathrm{HI} = \mathrm{C}_7\mathrm{H}_6\mathrm{O}_3 + \mathrm{I}_2$$

It is, therefore, evident that iodosalicylic acid cannot possibly be formed by the direct action of iodine upon salicylic acid, as Kolbe and Lautemann assert. Indeed, it is easy to see that the iodosalicylic and iodophenylic acids are produced by other reactions, and that nearly all that Kolbe and Lautemann state upon the formation of these acids, is based upon erroneous observations.

It would lead me too far to describe here all the experiments that I have made in order to throw some light upon the formation of the iodated acids described by Lautemann. I, therefore, confine myself to the following observations:—When salicylic acid is melted with iodine, or boiled with iodine and alcohol, no reaction takes place; and this explains why Lautemann could nowhere find the hydrogen which the salicylic acid must have necessarily eliminated. The iodosalicylic and the iodophenylic acids are formed by the process which Lautemann employed to separate the bodies which he fancied were already formed. In this process, two reactions must be distinguished, both of which lead to the formation of products containing iodine, of which fact I have convinced myself by special experiments.

When iodine acts upon an alkaline solution of a salicylate, iodosalicylic acids are principally formed, as also the red body described by Lautemann; at the same time, small quantities of iodophenylic acids are obtained. The formation of these products may be illustrated by the following formulæ:

$$C_7H_6O_3 + 3I_2 + 4KHO = \underset{\text{Red body.}}{C_6H_2I_2O} + CO_2 + 4H_2O + 4KI.$$

$$C_7H_6O_3 + I_2 + KHO = \underset{\substack{\text{Iodosalicylic}\\ \text{acid.}}}{C_7H_5IO_3} + H_2O + KI.$$

$$C_7H_6O_3 + 3I_2 + 3KHO = \underset{\substack{\text{Tri-iodophenylic}\\ \text{acid.}}}{C_7H_3I_3O} + CO_2 + 3H_2O + 3KI.$$

The second reaction by which products containing iodine may be produced from salicylic acid, is as follows:—When iodine acts upon salicylic acid in presence of iodic acid, salicylic acids containing iodine, and more especially iodo-substitution-compounds of phenylic acid, are formed.

We have for example:

$$5C_7H_6O_3 + 2I_2 + IO_3H = \underset{\substack{\text{Iodosalicylic}\\ \text{acid.}}}{5C_7H_5IO_3} + 3H_2O$$

$$5C_7H_6O_3 + 6I_2 + 3IO_3H = \underset{\substack{\text{Tri-iodophenylic}\\ \text{acid.}}}{5C_6H_3I_3O} + 5CO_2 + 9H_2O.$$

That iodophenylic acids are the chief products of this reaction, is explained by the behaviour of salicylic acid and iodosalicylic acid to iodic acid. When salicylic acid is heated with water and iodic acid, decomposition takes place even below 100°, phenylic and carbonic acids being produced. It will be easily understood that, in both reactions, products containing iodine may be formed. The hydrogen of salicylic acid is not taken away by iodine, to form hydriodic acid, but is expelled in each reaction in the form of water. The conditions which prevent the formation of iodo-substitution-compounds by the direct action of iodine are consequently evaded.

### *On the action of Hydriodic Acid upon Polyatomic Acids.*

The observations above enumerated lead to a simple theory of the beautiful reaction first brought into use by Lautemann, which has since rendered possible the reduction of many organic acids. The reduction caused by hydriodic acid is explained in the following manner: The reaction takes place by two stages; in the first stage, hydriodic acid produces a hydriodic ether, with elimination of water, that is to say, an iodo-substitution-compound of the same series of oxidation, containing less oxygen. In the second stage, this product of substitution by iodine is carried over into the normal substance by hydriodic acid acting by inverse substitution.

We have for example :

$$\underset{\text{Glycollic acid.}}{C_2H_4O_3} + HI = H_2O + \underset{\text{Iodacetic acid.}}{C_2H_3IO_2}$$

$$\underset{\text{Iodacetic acid.}}{C_2H_3IO_2} + HI = I_2 + \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

If we take into consideration that iodacetic acid is attacked even by dilute hydriodic acid at a low temperature, whereas the action of hydriodic acid on glycollic acid evidently does not take place, except under the same conditions as with hydrobromic acid (that is to say, by using a concentrated solution, and by heating), it is easy to perceive that the iodacetic acid which is formed as intermediate product, cannot be detected. It is evident that in all such reactions, no matter in what proportions the substances in question may be employed, the intermediate products can be detected only when they are less easily attacked by the reagent employed than the original substance. It will be further more comprehensible why only polyatomic acids whose basicity is less than their atomicity, are reduced by hydriodic acid. The reduction necessitates the formation of a hydriodic ether (an iodo-substitution-compound), and can, therefore, take place only with substances which contain alcoholic hydro[illegible]

I will finally observe that the typical re[illegible]ion above mentioned,

$$HI + HI + H_2 + I_2$$

which can be more generally expressed in the following form :

$$RI + R_1I = RR_1 + I_2,$$

appears to me to be susceptible of a further extension in various directions. I may perhaps be permitted to mention here some of the experiments on which I am at present engaged. Hydriodic acid may be allowed to act upon bodies which do not contain oxygen; retrograde substitutions would then be produced as follows :

$$\underset{\text{Iodoform.}}{CHI_3} + HI = I_2 + \underset{\text{Iodide of methylene.}}{CH_2I_2}$$

$$\underset{\text{Iodide of ethylene.}}{C_2H_4I_2} + HI = I_2 + \underset{\text{Iodide of ethyl.}}{C_2H_5I.}$$

Organic iodides may be employed instead of hydriodic acid, and thus syntheses similar to the following may probably be realised:

$$\underset{\text{Iodide of ethylene.}}{C_2H_4I_2} + \underset{\text{Iodide of methyl.}}{CH_3I} = I_2 + C_2H_4\,(CH_3)I = I_2 + \underset{\text{Iodide of trityl.}}{C_3H_7I.}$$

$$\underset{\text{Iodacetic acid.}}{C_2H_3IO_2} + \underset{\text{Iodide of methyl.}}{CH_3I} = I_2 + C_2H_3\,(CH_3)O_2 = I_2 + \underset{\text{Propionic acid.}}{C_3H_6O_2}$$

$$\underset{\text{Iodoacetic acid.}}{C_2H_3IO_2} + \underset{\text{Iodide of acetyl.}}{C_2H_3OI} = I_2 + C_2H_3(C_2H_3O)O_2 = I_2 + C_4H_6O_3$$

---

## XXV.—*On the Classification of the Elements in relation to their Atomicities.*

By Professor WILLIAMSON, F.R.S., &c., President of the Chemical Society.

I AM desirous of bringing under the consideration of the Society, some of the chemical grounds for doubling the atomic weights of all the metals in Gerhardt's system of atomic weights, excepting the alkali-metals, silver, gold, boron, and the metals of the nitrogen series,—a change which has been proposed, mainly on physical grounds, by Caninzzaro, and which seems to be obtaining the approbation of a greater and greater number of chemists.

It is now about twenty years since Gerhardt drew attention to the error of the molecular weights, or equivalent weights as he called them, which represented water as consisting of one atom of oxygen and one of hydrogen, and proposed to double the atomic weight of oxygen and of carbon.

If Gerhardt had taken Berzelius' atomic weights, and, while translating them into the hydrogen scale, had halved the atomic weights of the alkali-metals and boron, he would have given us at once the system which we now adopt, saving the rectification of a few formulæ, such as that of silica and of oxide of uranium, whereas, by merely doubling oxygen, sulphur, selenium and carbon in the then existing system of atomic weights, he really introduced a system in which there are between thirty and forty atomic weights to correct, instead of one which needed only five or six such corrections. It would be unreasonable to apply this fact in any degree to the disparagement of Gerhardt's work. It only shows how tortuous is the road which leads to truth.

The discussion of the question involves chiefly the consideration of the classification of the elements, under the respective heads of chlorine and of oxygen, the first tribe containing those elements an atom of which combines with one atom of hydrogen or chlorine, or with three, or with five, &c., whilst the second tribe contains elements, each atom of which combines with two atoms of chlorine, or other monads, or with four or six, &c. I do not, however, recommend that the two great classes of elements be thus distinguished from one another: for our chief evidence of atomic weight is derived from the study of the molecular weights of compounds, and the molecule is the unit to which we must refer our results.

The first class is best described as furnishing only an even number of atoms to each molecule, whereas the second class sometimes furnishes an even, sometimes an uneven number of atoms to one molecule.

### 1. *Class of Elements which furnishes an even number of Atoms to each Molecule.*

H = 1
Fl = 19
Cl = 35·5
Br = 80
I = 127

Li = 7
Na = 23
K = 39
Rb = 85
Cs = 133
Tl = 203
Ag = 108

N = 14
P = 31
As = 75
Sb = 122
Bi = 210
B = 11
Au = 196

### 2. *Class of Elements which furnishes either odd or even number of Atoms to a Molecule.*

O = 16
S = 32
Se = 79·5
Te = 129
Ca = 40
Sr = 87·5
Ba = 137

G = 9
Y = 64
Ce = 92
La = 92
Di = 96
U = 120
Zr = 89·5

C = 12
Si = 28
Sn = 118
Ti = 50
Mo = 96
V = 137
W = 184

Pb = 207
Hg = 200
Mg = 24
Zn = 65
Co = 112
Al = 27·5
Fe = 56
Cr = 52·5
Mn = 55
Co = 58·5
Ni = 58·5
Cu = 63·5

Ta = 138
Nb = 195
Th = 238

Pt = 197
Ir = 197
Os = 199
Ro = 104
Ru = 104
Pd = 106·5

The process of classifying the elements has followed the very natural order, of establishing a certain number of well-defined families, subsequently connected together by erratic members, which occasionally left their usual places to go over to some neighbouring families. Chlorine, bromine, and iodine have long been acknowledged to constitute a natural family, and there are some, though hardly sufficient reasons, for placing fluorine at its head. The three elements have the same vapour-volume as hydrogen in the free state, and we accordingly represent their respective molecules as $Cl_2$, $Br_2$, $I_2$, corresponding to $H_2$ = two volumes. They form hydrides of similar composition and analogous properties, and of the same vapour-volume. Their compounds with most metals are analogous, and have the same atomic heat and general crystalline form. Their corresponding oxygen-acids also exhibit considerable analogy. With organic radicles they form neutral ethers, like $ClC_2H_5$, $ClC_2H_3O$, and no acid ethers. So that, when oxygen, in a molecule of alcohol or of acetic acid, is replaced by chlorine, two atoms of chlorine take the place of one atom of oxygen, and give rise to a molecule of chloride of ethyl and a molecule of hydrochloric acid:

$$\underset{\text{Alcohol.}}{C_2H_6O} + Cl_2 - O = \underset{\substack{\text{Chloride of}\\ \text{ethyl.}}}{C_2H_5Cl} + HCl.$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + Cl_2 - ClH = \underset{\text{Chloracetic acid.}}{C_2H_3ClO_2}.$$

$$\underset{\text{Chloracetic acid}}{C_2H_3ClO_2} + Cl_2 - HCl = \underset{\text{Bichloracetic acid.}}{C_2H_2Cl_2O_2}.$$

They replace hydrogen, atom for atom, taking out one, two, or three atoms, &c., according to circumstances. Their hydrogen-compounds are all monobasic acids; for if in a given quantity of hydrochloric or hydriodic acid, we replace part only of the hydrogen by potassium, we get at once a neutral salt mixed with the remaining acid, which is undecomposed, and never an acid salt of the alkalies. Fluorine in this respect exhibits an anomaly which tends to remove it from this family to a biatomic one: for the acid fluoride of potassium is a well-defined compound of considerable stability, the existence of which points to the atomic weight 38 for fluorine, and the formula $H_2F$ for hydro fluoric acid.

Hydrofluoric acid, moreover, combines with various metallic fluorides, such as fluoride of silicon and fluoride of boron. Similar double salts are, however, formed by chlorine—for instance, terchloride of gold combines with a molecule of hydrochloric acid, or of an alkaline chloride; tetrachloride of platinum combines with two molecules of hydrochloric acid, or of chloride of potassium, &c.; and from the numerous family of double chlorides and bromides, &c., the following few may be mentioned by way of illustration :—

$Al\ K\ Cl_4$
$Cu\ K_2\ Cl_4$
$Zn\ K\ I_3$
$Pt\ H_2\ Cl_6$
$Pt\ K_2\ Cl_6$
$Pt\ K_2\ Cl_4$
$Au\ K\ Cl_4$
$Sn\ K_2\ Cl_6$
$Sn\ K_4\ Cl_6\ (H_2O)_3$

Now it is not possible to reconcile the constitution of these various bodies with one another, and with the simpler compounds of chlorine, by any theory representing that element as polyatomic, and as holding together the metallic atoms in their salts in virtue of its polyatomic character.

On the other hand, hydrochloric acid and metallic chlorides of opposite properties cannot be assumed to be incapable of uniting with one another, while it is well known that oxides of basylous properties unite with those of chlorous properties. Hydrochloric acid unites with ammonia, and we do admit that the two molecules are bound together into one, by a chemical force of combination, and not by any tetratomic character of the hydrogen; and HCl or KCl combines with $O_3$ by a similar force.

Again, oxygen, sulphur, selenium, and tellurium are admitted to be truly analogous elements: for the parallelism of oxygen-salts and sulphur-salts affords abundant proof of the analogy of oxygen and sulphur; and the molecular volumes of sulphur and selenium are found by Deville to agree at high temperatures with that of oxygen.

The elements, selenium and tellurium, form acids analogous to sulphurous and sulphuric acids respectively. When combined with organic radicles, they form compounds of the same molecular volume in the form of vapour, and when any one of them, such as oxygen, replaces hydrogen in an organic body, it takes out two atoms of hydrogen at a time, replacing each couple by one atom of oxygen, as in the formation of acetic acid from alcohol:

$$\underset{\text{Alcohol}}{C_2H_6O} + O_2 - H_2O = \underset{\text{Acetic acid.}}{C_2H_4O_2}.$$

When we partially decompose water by potassium, we get hydrate of potash formed, which is a molecule of water from which half the hydrogen is expelled and replaced by potassium, and a second atom of potassium is required to displace this remaining hydrogen.

If we compare any protochloride with a corresponding oxide, either of a metal or organic radicle, we find that the molecule of the oxide contains twice as many equivalents of the metal or radicle as the chloride, and that one atom from the oxygen-family is equivalent to two atoms from the chlorine-family:

$$\underset{\substack{\text{Iodide of}\\ \text{ethyl.}}}{C_2H_5I} + HKS - KI = \underset{\text{Mercaptan.}}{C_2H_6S}.$$

When oxygen in alcohol is replaced by sulphur, no breaking up into sulphide of ethyl and sulphide of hydrogen takes place, as when the oxygen is replaced by chlorine or bromine.

Among the best known compounds there are several, one atom of which combines, like an atom of oxygen or of sulphur, with two atoms like hydrogen or chlorine. Thus carbonic oxide, sulphurous acid and ethylene are capable of combining, in the proportion of one atom of the radicle, with two atoms of chlorine, forming the compounds $COCl_2$ phosgene, $SO_2Cl_2$ chloro-sulphuric acid, and $C_2H_4Cl_2$ chloride of ethylene, or Dutch liquid, and these molecules have the same vapour-volume as steam $OH_2$. But in the free state, the radicles have a vapour-volume twice as great as the equivalent quantity of oxygen, the atoms $CO_2$, $SO_2$, $C_2H_4$ being as bulky as $O_2$; so that, whereas the molecule of oxygen and of sulphur consists of two atoms, that of carbonic oxide consists of one atom only, and the molecules of sulphurous acid and of ethylene consist of one atom each respectively.

Another family of very marked characteristics is that consisting of N, P, As, Sb, Bi, each member of which combines with three atoms of hydrogen or of ethyl ($C_2H_5$), forming a basic compound analogous to ammonia. Their analogy in chemical reactions is also well known, as each of them forms an oxide corresponding to nitrous acid, and another corresponding to nitric acid.

The sulphides of arsenic and antimony are notorious for their great resemblance, and that of arsenious acid and antimonious acid is scarcely less striking: it even extends to isomorphism. Then again, phosphoric and arsenic acids exhibit an almost perplexing resemblance, and isomorphism of their corresponding salts.

The atomic heat of the last four terms of the series is also very nearly the same, whilst that of nitrogen (examined of course as a gas) is considerably less. Then the molecule of phosphorus and of arsenic in the state of vapour consists of four atoms, whilst that of nitrogen consists of two, showing a variety of constitution which is by no means to be wondered at, when we recollect that these elements are not necessarily triatomic, but sometimes monatomic, pentatomic, &c., so that the molecule of free nitrogen consists of two monatomic atoms or two triatomic, whilst the molecule of phosphorus, and of arsenic, is formed on the ammonia type of one triatomic atom and three monatomic atoms.

Another family may perhaps be made up of carbon and silicon, both of which form volatile tetrachlorides, and are sometimes biatomic, sometimes tetratomic in their acids.

In a recent note published in the *Comptes rendus*, Prof. Kekulé appears to express an opinion that the atomicity of each element must be regarded as unchangeable. For the present, however, I cannot see any advantage in representing, as that distinguished chemist proposes to do, terchloride of iodine as $ICl.Cl_2$, pentachloride of phosphorus as $PCl_3.Cl_2$; for by the same right, proto-iodide of phosphorus would be $PI_3 - I_2$, and nitrous oxide would be $N_2O_3 - O_2$, a change of form which might serve to turn aside the attention of chemists from the fact of the different atomicity of the elements I, N, and P in those compounds, and in ICl, $PCl_3$, $N_2O_3$, but which would neither remove the fact nor explain it. When any element is combined with a radicle, we of course view the compound as analogous to that of the same element with another of the same atomicity as the radicle. The chloride of ethyl is of course analogous to hydrochloric acid, and is not a compound in which chlorine has nonatomic functions. In each of the compounds $N_2O$, $N_2O_3$, $N_2O_5$, nitrogen has a different atomicity from the others. Thallium and gold also form perfectly well-defined protochlorides and terchlorides showing a similar change of atomicity.

Among metals, lithium, sodium, potassium, and probably also the new metals, rubidium, cæsium, and thallium, have many important points of resemblance, which show them to be monatomic. Thus they replace hydrogen, atom for atom, and form with many bibasic acids, both normal and acid salts. Their chlorides form with tetrachloride of platinum, analogous double salts, of insolubility increasing with the atomic weight of the metal, and their sulphates form with sulphate of alumina, &c., those well-characterised salts called alums. They do not form basic salts (unless when triatomic, like thallium). They have nearly the same atomic heat.

Silver is remarkable for several of the properties which we have noticed in the alkali-metals. It is eminently monatomic, and disinclined to form basic salts. Its atomic heat also shows it to be monatomic. It is said to form an alum; and its sulphate has a great resemblance of form to the anhydrous sulphate of soda. Gold, also, must from its specific heat, and the constitution of its two chlorides, be classed among the metals which are monatomic or triatomic. Boron is evidently triatomic in its best known compounds, as proved by its terchloride and ter-ethylide.

Among metals with strongly basylous properties, calcium, strontium, barium, and lead, are connected by very close analogies. The general resemblance of their sulphates and carbonates, and the isomorphism of most of them, are too well known to need mention.

But lead has been obtained in combination with ethyl, and the compound $Pb\,(C_2H_5)_4$, which corresponds to binoxide of lead, in which the 2 atoms of oxygen are replaced by 4 atoms of ethyl, and the compound $Pb\,(C_2H_5)_3Cl$, prove beyond a doubt that the metal is there tetratomic.

Again, lead is preeminent for its tendency to form basic salts, even with purely monatomic chlorous elements or radicles. Thus ordinary nitrate of lead, when warmed in aqueous solution with white lead, expels carbonic acid from that compound, and forms the well-known and crystallisable basic nitrate $Pb\left\{\begin{matrix}NO_3\\HO\end{matrix}\right.$. If we represent this salt upon the water-type, it is formed from 2 molecules of water $\left.\begin{matrix}\begin{matrix}H\\H\end{matrix}O\\\begin{matrix}H\\H\end{matrix}O\end{matrix}\right\}$ two atoms of hydrogen, one from each molecule, being replaced by the biatomic atom lead, whilst one of the remaining atoms of hydrogen is replaced by $NO_2$, forming the compound $\left.\begin{matrix}NO_2\\Pb\\H\end{matrix}\begin{matrix}O\\O\end{matrix}\right\}$. But if we adopt the binary theory, we must represent it as lead combined with the radicle $NO_3$, and also with the radicle $HO$; and the biatomic lead holds these atoms together, just as much as biatomic oxygen holds together ethyl and hydrogen in alcohol; and if we mix our lead-compound with sulphate of silver and heat with water, we replace the one atom of lead in it by 2 atoms of silver, getting a mixture of nitrate of silver and brown hydrated oxide of silver, just as the replacement of oxygen in alcohol by $Cl_2$ forms chloride of ethyl and hydrochloric acid:

$$PbNO_3HO + SO_4Ag_2 - SO_4Pb = AgNO_3 + AgHO.$$

We are thus led to consider these metals as biatomic, and to represent their oxides by the old formulæ $CaO$, $SrO$, $BaO$, $PbO$, whilst their carbonates, sulphites, and sulphates have formulæ like $CaCO_3$, $CaSO_3$, $CaSO_4$, and their chlorides, nitrates and phosphates, have formulæ like $CaCl_2$, $Ca(NO_3)_2$, $Ca_3(PO_4)_2$.

Nitrate of potash has thus a similar formula ($NO_3K$) to arragonite $CO_3Ca$, and their isomorphism is no longer surprising. The same remark applies to calc-spar and nitrate of soda.

Another analogous group of metals is the triad, magnesium, zinc and cadmium, all volatile, and forming salts which greatly resemble one another, and are, in many cases isomorphous. The constitution and properties of Frankland's zinc-ethyl leave no doubt of the biatomic character of zinc: for the compound $Zn(C_2H_5)_2$ has the same molecular volume as ether, and if the atom of zinc were taken out and replaced by an atom of oxygen, there would be no change of volume. Then half the ethyl in zinc-ethyl is replaceable by iodine, just as half the ethyl in ether is replaceable by potassium.

Having thus established the biatomic character of this family, we can extend the conclusion to the other metals which form magnesian-oxides, so called from the striking analogy of constitution of several of their salts, to the corresponding salt of magnesia. In this manner we are led to adopt for iron, manganese, nickel, cobalt, and copper, atomic weights corresponding to biatomic characters. The subsulphide of copper is thus represented by the formula $Cu_2S$, which is sufficiently similar to that of sulphide of silver $Ag_2S$, to remove our surprise at their isomorphism.

There is, moreover, in the reactions of alumina, sesquioxide of iron, sesquioxide of chromium, and sesquioxide of manganese, much resemblance. All of them are weak bases, and their sulphates form, with sulphate of potash, those most characteristic salts called *alums*.

The first three are isomorphous in the uncombined state, so that the conclusion which we have established for iron and manganese, may be extended to aluminum and chromium. But it is also arrived at by other means: for chromium, in combination with oxygen and chlorine, forms the well characterized compound $CrO_2Cl_2$, chlorochromic acid, which contains the same quantity of oxygen and of chlorine as chlorosulphuric acid, in two volumes of vapour, having 52·5 parts by weight of chromium in the place of the 32 of sulphur of that compound. Again, chromic and sulphuric acids exhibit a marked resemblance of properties, the former being, if anything, even more distinctly bibasic than the latter; and their normal potash-salts are isomorphous, so that chromium is abundantly proved to be similar to sulphur in atomicity, and brings in evidence of its own in favour of the biatomic character of aluminum, iron and manganese. In like manner, manganese in manganic acid, is connected with sulphur in sulphuric acid, and requires a corresponding atomic weight. The isomorphism and general analogy of permanganate of potash with perchlorate of potash, has often been alluded to as pointing to the necessity of representing the former by a formula containing one large atom of manganese $MnO_4K$; but although this formula, by assimilating the expressions for these two similar bodies, removes one difficulty, it creates at the same time another, by presenting us with a formula containing only 1 atom from the first family of elements. I will not hazard any opinion at present regarding the propriety of removing this difficulty, by doubling the above formula, together with that of perchlorate of potash, although I may remark, that the constitution of the basic periodate of soda points to the formula $I_2O_9Na_4.3(H_2O)$. The same difficulty exists with respect to alum and its congeners: for the simplest formula $AlK(SO_4)_2(H_2O)_{12}$, is open to the same objection as that of permanganate of potash.

An exceedingly strong ground for admitting for many heavy metals the atomic weights corresponding to a biatomic character, was brought forward some time ago by Wurtz, who pointed out that, adopting for oxygen the atomic weight 16, we get a half molecule of water $\frac{H_2O}{2}$ in one molecule of various salts, if we consider the metals monatomic.

Other metals are susceptible of reduction by similar analogies to the class of elements which are biatomic or tetratomic, &c. Thus mercury is proved, by the ethylide and methylide, to be biatomic, by the fact that the compound of one atom of mercury with two atoms of ethyl or of methyl $\begin{matrix}CH_3\\CH_3\end{matrix}Hg$ = two vols. occcupies the same volume in the state of vapour as the compound of one atom of oxygen with two of ethyl or of methyl; and we can take out one atom of methyl from the bimethylide of mercury, and replace it by an atom of chlorine, bromine, or iodine, without disturbing the type $\begin{matrix}CH_3\\I\end{matrix}Hg$. The common bichloride of mercury has moreover a vapour-volume corresponding to the biatomic character of the metal; and the same thing holds good of the vapour of metallic mercury itself, which has the same volume as the metal cadmium, and probably zinc, and the well known biatomic radicles $CO$, $SO_2$, $C_2H_4$, but double the volume of the elements oxygen and sulphur. In the present state of our knowledge, I am not aware of any sufficient grounds for deciding which of these two constitutions of the free molecule of a biatomic element or radicle is to be considered as normal, and which is abnormal. On the one hand, mercury, cadmium, and all known biatomic radicles have a molecule containing one atom, whilst the molecule of oxygen contains two atoms, and that of sulphur two at high temperatures, and six at lower temperatures. Selenium is at high temperatures like sulphur.

It has been amply shown by Dr. Odling and others, that tin is biatomic and tetratomic in its two chlorides; and its compounds with the organic radicles, chlorine, &c., leave no room for doubt on the point.

I will not detain the Society on this occasion by attempting an analysis of the various chains of evidence by which the remaining metals can be shown to belong to the great biatomic class containing already so many; for the evidence, as far as I know it, is a repetition of analogies similar to those above considered in the cases of some of the best known elements.

The vapour-densities of the so-called sesquichlorides of iron, aluminum, and chromium, as determined by Deville, show that the molecule of each of these bodies contains two atoms of metal and six atoms of chlorine, in fact the same quantity of metal as the molecule of the sesqui-oxide; and this fact has been held to be an anomaly, from the point of view adopted regarding their atomic weights. I believe, however, that it is far from being anomalous. These vapour-densities are the least that can be reconciled with our conclusion that the metals permanently combine with even numbers of atoms from the first family in each molecule. For if one atom of iron could on occasion combine with three atoms of chlorine, to form one molecule, our law respecting it would assume the not very wise form: that iron combines with an even number of atoms from the first family, except when it combines with an uneven number.

The fact is that the sesquichlorides are not exceptions to the law, as at first sight they are suspected of being. Precisely the same remarks apply to the so-called subchloride of sulphur, the molecule of which is $S_2Cl_2$, as required by the law. So also cyanogen $C_2N_2$, acetylene $C_2H_2$, ethyl $C_4H_{10}$, &c.

Amongst exceptions, I must however mention nitric oxide and calomel, both of which have vapour-densities corresponding to the molecular formulæ NO and HgCl, which are to me at present simply unintelligible.*

Many compounds are known to undergo decomposition on evaporation, and to be reproduced on condensation; thus $NH_5O$ yields the two molecules $NH_3$ and $H_2O$, each with its own volume; so also $SO_3H_2$ yields $SO_2$ and $H_2O$. $SO_4H_2$ and $PCl_5$ are also known to yield on evaporation vapours corresponding to a breaking up into two molecules; and there are strong reasons from analogy, as well as experimental evidence, to believe such decompositions. As however a high authority seems inclined to doubt the decomposition, the matter may be considered as still *sub judice.*

---

* Since the above was written, Dr. Odling has suggested an excellent explanation of the vapour-density of calomel, as being really that of an atom of mercury mixed with a molecule of bichloride of mercury. He has also since informed me that he finds evidence of the presence of metallic mercury in the vapour of calomel by its action on gold-leaf, and that bichloride of mercury is deposited from the vapour of calomel.

The existence of basic salts of mercury or copper, when apparently monatomic, is another class of apparent exceptions to the law. For, if in the subnitrate of mercury, the atom of metal really replaced one atom of hydrogen, just as potassium does in nitrate of potash, there ought not to be a basic subnitrate of mercury, any more than a basic potash-salt; whereas, if the subnitrate of mercury, $Hg_2(NO_3)_2$, contains, as I assert, in one molecule, two atoms of metal and two atoms of the salt-radicle of the nitrates $(NO_3)$, then a basic salt, $Hg_2NO_3HO$, is as natural and intelligible a compound as the basic nitrate of the red oxide.

The action of ammonia on calomel confirms the molecular weight, $Hg_2Cl_2$, for calomel: for the compound $NH_2Hg_2Cl$ formed simultaneously with sal-ammonia proves that twice $(HgCl)$ takes part in the reaction.

## XXV.—*On the Constitution of Wood-spirit.*

By William Dancer, Dalton Scholar in the Laboratory of Owens College Manchester.

The chemical constitution of certain volatile substances which occur in crude wood-spirit, together with varying quantities of methyl-alcohol, acetone, and acetate of methyl, has, up to the present time, remained extremely doubtful. The body called lignone by Gmelin, and xylite by Weidmann and Schweizer, has been shown by Voelckel* to be a mixture of several of the above-named bodies, together with a supposed new body, having the formula $Ȼ_6H_{12}Ɵ_2$, and boiling at 61° C., for which he proposes to retain the name of xylite.

The methods employed by Voelckel for the isolation of this body are not much better than those used previously by Weidmann and Schweizer, and consist of treatment with chloride of calcium and subsequent fractional distillation. From the close approximation of the boiling points of acetone, acetate of methyl, and methyl-alcohol, it appears impossible that repeated fractional distillation can effect a perfect separation from a mixture of these, of any fourth body boiling about 60° C. At the suggestion of Professor Roscoe, I therefore undertook an examination of the subject, with the view of applying to the mixture more effectual methods of separation than had previously been employed. The following is an outline of the process adopted. Crude wood-spirit having been well dried over quicklime, was distilled upwards for some time with a concentrated solution of caustic soda, and thus the greater portion of the acetate of methyl was decomposed; the distillate was then repeatedly treated with chloride of calcium, until no further formation of the alcohol-compound occurred. The acetone was next separated by repeated treatment with saturated solution of bisulphite of sodium, whilst, to insure the complete removal of the acetate of methyl, the residual liquid was distilled upwards with caustic potash until the brown coloration ceased. It was afterwards acted upon with chloride of calcium, to retain the methyl-alcohol formed by the decomposition of the acetate. In this way a liquid was obtained, from which neither chloride of calcium nor potash removed any further impurities; this liquid boiled between 55° and 70° C.; it was easily oxidised by dilute nitric acid and blackened by oil of vitriol. On the first treatment with sodium, hydrogen was evolved and a brown resinous substance formed; but after a few distillations over this metal, a liquid was obtained upon which sodium had no further action whatever. This liquid, which possessed a peculiar acetal-like smell, and boiled at 63°—64° C. is, as the following analyses show:—

---

* Pogg. Ann., lxxxiii. 272, 557.

Bimethyl-acetal $\left.\begin{matrix}C_2H_4\\2(CH_3)\end{matrix}\right\}O_2$

1. 0·2928 grm. of the liquid gave 0·57045 grm. carbonic acid, and 0·29735 grm. water.
2. 0·3117 grm. gave 0·6119 grm. carbonic acid, and 0·3352 grm. water.
3. 0·3059 grm. gave 0·6000 grm. carbonic acid, and 0·3040 grm. water.

| | | Calculated. | Found.<br>I. | <br>II. | <br>III. |
|---|---|---|---|---|---|
| $C_4$ | = | 53·33 | 53·13 | 53·53 | 53·49 |
| $H_{10}$ | = | 11·11 | 11·28 | 11·94 | 11·04 |
| $O_2$ | = | 35·56 | 35·59 | 34·53 | 35·47 |
| | | 100·00 | 100·00 | 100·00 | 100·00 |

The following numbers were obtained for the vapour-density:—

| | |
|---|---|
| Weight of bulb, with air, at temperature 9° C. | 8·7962 grms. |
| Weight of bulb and vapour, at temperature 9° C. | 8·9435 grms. |
| Capacity of bulb.................... | 93·2 cub. cents. |
| Temperature at time of sealing bulb .. | 121° C. |

These numbers give the vapour-density as 3·165, which closely corresponds with the calculated number 3·114.

The specific gravity of the liquid at 0° C. compared with that of water at 4° C. is

Sp. gr. at 0° C.. = 0·8787.
„ 14 C°.. = 0·8590.
„ at 22 C° = 0·8503.
„ at 23 C° = 0·8197.
„ at 25 C° = 0·8176.

Bimethyl-acetal was first prepared by Wurtz* by acting on a mixture of equivalent quanties of methyl- and ethyl-alcohols with sulphuric acid and binoxide of manganese. In order to compare the properties of the bimethyl-acetal prepared by the two methods, I obtained pure methyl-alcohol from the oxalate, and on heating this together with vinic alcohol, in the above-mentioned way, I obtained bimethyl-acetal as a liquid agreeing with Wurtz's description of this body, and possessing identical properties with that contained in the crude wood-spirit.

The quantity of bimethyl-acetal contained in crude wood-spirit appears to vary considerably, 20 grms. of this substance being obtained from 2 litres of one sample, whilst the same quantity of another yielded only 10 grms.

From these experiments, it appears that crude wood-spirit consists of a mixture of varying proportions of methyl-alcohol, acetone, acetate of methyl, and bimethyl-acetal, and that the supposed lignone or xylite has no real existence.

---

* Ann. Ch. Phys. [3], lxxxiii, 370. The boiling point of this compound is stated in the original paper to be 65° C.; that given for it in Kekulé's and Limpricht's Handbooks, being a misprint, evidently originating in the Annalen der Chemie und Pharmacie.

# XXVII.—*On Chlorophosphuret of Nitrogen, and its Products of Decomposition.*

By J. H. Gladstone, Ph. D., F.R.S., and J. D. Holmes, Esq.

Under this same title, two papers were communicated by one of us to the Chemical Society in 1850, and were published in vol. iii. of the Quarterly Journal, pp. 135 and 353. The general result was to confirm the formula $P_3N_2Cl_5$ assigned to chlorophosphuret of nitrogen by its discoverers, Wöhler and Liebig, to describe the substance more fully, and especially to show that, under the influence of aqueous ether, alkalies, and even of water, it was capable of giving rise to two new acids, named respectively *deutazophosphoric* and *azophosphoric* acids. The first was believed to be produced by the simple decomposition:

$$P_3N_2Cl_5 + 8HO^* = 3HO.P_3N_2O_5 + 5HCl;$$

but neither the acid nor its salts could be obtained in a state to give trustworthy analyses. The second—azophosphoric acid—is produced from a solution of a deutazophosphate by heating it with different metallic salts, when a precipitate containing the new acid falls. The most remarkable of these is a ferric salt, insoluble in dilute acids, and soluble in ammonia; but several others were prepared, described, and analysed, and the common formula found for them was $3MO.P_2NO_5$, combined with from two to five equivalents of water.

But these formulæ were soon challenged. Laurent, in the *Comptes Rendus* for Sept. 9, 1850, considers that chlorophosphuret of nitrogen must have the formula $PNCl_2$, and the two acids derived from it must be respectively $P_2N_2H_6\Theta_5$ and $P_2NH_5\Theta_6$, according to the following schemes of decomposition:

$$\begin{gathered} PCl_5 + NH_3 = PNCl_2 + 3HCl \\ 2(PNCl_2) + 5H_2\Theta = P_2N_2H_6\Theta_5 + 4HCl \\ P_2N_2H_6\Theta_5 + H_2\Theta = P_2NH_5\Theta_6 + NH_3; \end{gathered}$$

and he views these acids as amidated acids, giving them corresponding names, while their discoverer regarded them as $3HO.PO_5$ conjugated with PN and 2PN.

---

* In this paper we have been obliged to employ both the systems of notation, therefore when the equivalent of oxygen is 16, we have distinguished it by the bar frequently used for that purpose.

The opposite views of their composition are therefore as follows, giving only empirical formulæ:

| GLADSTONE. | | | LAURENT. |
|---|---|---|---|
| Chlorophosphuret of nitrogen | $P_3N_2Cl_5$ | $PNCl_2$ | Chlorophosphuret of nitrogen |
| Deutazophosphoric acid | $P_3N_2H_3O_8$ | $P_2N_2H_6\Theta_5$ | Pyrophosphodiamic acid |
| Azophosphoric acid | $P_2NH_3O_8$ | $P_2NH_5\Theta_6$ | Pyrophosphamic acid |

Laurent did not examine the substances himself, and the results of the analysis published in the Quarterly Journal, were almost as compatible with the one view as with the other; but the following considerations led the original discoverer of the acids to retain confidence in his own formulæ:—It was hardly conceivable that the chlorophosphuret of nitrogen was produced by so simple a reaction as that given in Laurent's equation; for in that case the whole of the pentachloride would have suffered that transformation; or if some other reaction had been set up, the amount of chlorophosphuret would have varied with different conditions, whereas the proportion actually found is very small, and apparently very uniform. Again, in the conversion of deutazophosphoric into azophosphoric acid, on the first theory, only two-thirds of the phosphorus should be found in the new precipitate, while, on the supposition of Laurent, the whole should be found there; but in a recorded experiment the proportion so found was just two-thirds.

Yet the subject was evidently one that deserved re-examination, and Dr. Gladstone always intended to revert to it at some time or other; but the difficulty of preparing a quantity of the substances, and of analysing them when prepared, caused him to defer this in favour of more promising lines of research.

In the mean time Schiff,* examining the action of ammonia on anhydrous phosphoric acid, found the principal product to be an acid, which he considered to be identical with deutazophosphoric acid; but he gave it a third name—phosphamic acid, and expressed the reaction thus:—

$$\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O_6 + 2NH_3 = 2\left(\left.\begin{matrix}NH(PO_2)\\H\end{matrix}\right\}O_2\right) + 2HO.$$

---

* Ann. Ch. Pharm., ciii, 168.

He prepared and analysed the salts of barium, calcium, iron, and nickel, and described some others, giving them the general formula $PNHMO_4$, sometimes with $2HO$.

In relating the experiments we have recently made on this subject, we shall give first the synthetical, and afterwards the analytical results :—

## SYNTHETICAL RESULTS.

*Chlorophosphuret of Nitrogen.*—Our first attempt was to discover some more productive method of preparing chlorophosphuret of nitrogen than those hitherto known, viz., saturating pentachloride of phosphorus with ammoniacal gas, or heating it with chloride of ammonium. In this we were unsuccessful, though we found one reaction by which its preparation is rather more easily effected. If "white precipitate" ($NHg_2H_2Cl$) be intimately mixed with the pentachloride of phosphorus in a flask, and gently heated, a brisk action ensues, and chlorophosphuret of nitrogen is formed, mixed with chlorophosphamide, chloride of mercury, and chloride of ammonium. When treated with water, the two latter substances dissolve, and from the residue when dry the chlorophosphuret may be extracted by means of ether, chloroform, or bisulphide of carbon.

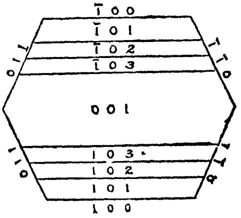
We are enabled to add to the description of the physical properties of this body previously given, the following account of its crystalline form and optical properties, kindly furnished by Prof. W. H. Miller, of Cambridge.

"Prismatic: 101, 001 = 61° 38′; 110, 100 = 66° 14′.

Observed forms: 001, 100, 103, 102, 101, 401, 110, 210.

Angles:

| | | |
|---|---|---|
| 401, | $\bar{4}01$ | 164° 38′ |
| 101, | 101 | 123° 16′ |
| 102, | $\bar{1}02$ | 85° 36′ |
| 103, | $\bar{1}03$ | 63° 22′ |
| 110, | $\bar{1}10$ | 47° 32′ |
| 210, | 210 | 82° 44′ |
| 001, | 401 | 82° 19′ |
| 001, | 101 | 61° 38′ |
| 001, | 102 | 42° 48′ |
| 001, | 103 | 31° 41′ |



| | | |
|---|---|---|
| 001, | 110 | 90° 0′ |
| 001, | 210 | 90° 0′ |
| 001, | 100 | 90° 0′ |
| 100, | 401 | 7° 41′ |
| 100, | 101 | 28° 22′ |
| 100, | 102 | 47° 12′ |
| 100, | 103 | 58° 19′ |
| 100, | 110 | 66° 14′ |
| 100, | 210 | 48° 38′ |

“An appearance resembling cleavage parallel to the face 0 0 1, was observed in one crystal; but as no cleavage could be detected in the other crystals examined, it was probably due to the existence of a plane of union.

“ Approximate values of the optical constants were obtained by observing the apparent angle between the optic axes, as seen through two opposite faces of the form 110; the minimum deviations of the brightest part of the solar spectrum; and the planes of polarization of the refracted rays through the faces 1 0 0, $\bar{1}$ 1 0, and through the faces 0 0 1, 1 0 0, the crystal being immersed in oil. It appears from these observations that, for a ray in the plane 0 0 1, and polarized in that plane, the index of refraction is between 1·616 and 1·617; that of the two rays in the plane 0 1 0, the more refrangible is polarised in that plane, and its index is between 1·633 and 1·634; and that the optic axes lie in the plane 0 0 1, making with one another an angle of 23° 20′, which is bisected by the line 0 1 0. Hence of the two rays in the plane 1 0 0, the less refrangible is polarised in that plane, and its index is a little less than 1·616.”

We have determined the specific gravity of the chlorophosphuret of nitrogen to be 1·98. Yet small crystals or a film of the melted substance will float on water, doubtless from its inability to be wetted.

The specific refractive energy of this compound, *i.e.*, the refractive index minus unity, divided by the density, will be ·316, a number approximating to that calculated from the specific refractive energies of its constituents, viz., ·332, taking that of phosphorus at ·58, of nitrogen at ·238, and of chlorine at ·242.

*Deutazophosphoric Acid.*—We have been more successful in obtaining this acid in considerable quantity; chlorophosphuret of nitrogen when decomposed by an alcoholic solution of an alkali, yields its full amount of the acid, mixed with an alkaline chloride. By two other methods it is more easily prepared in abundance.

The first is that discovered by Schiff, by the action of ammonia on anhydrous phosphoric acid. The white salt thus obtained, when dissolved in water, yields a neutral or slightly acid solution. This solution contains abundance of deutazophosphoric acid; as is shown by the formation of the very characteristic ferric azophosphate, when it is boiled with an iron salt, and by its agreement in every respect with the known properties of deutazophosphoric acid, as obtained from chlorophosphuret of nitrogen; but we could not obtain it free from metaphosphoric and possibly other acids.

The second process is by the action of dry ammonia on oxychloride of phosphorus, taking care that the temperature does not rise to any great extent. The action should be stopped as soon as the oxychloride is converted into a solid white substance. This substance, first observed by Wurtz, is perfectly soluble in water, the solution containing hydrochloric and deutazophosphoric acids partly as ammonium-salts. If this solution be exactly neutralized with ammonia, it produces precipitates of deutazophosphates with several metallic salts.

*Azophosphoric Acid.*—This acid is prepared from any solution containing free deutazophosphoric acid by simply heating it, but in this process the decomposition is apt to go too far, and phosphate of ammonium may be the only result. The preferable method is to prepare some azophosphate, which is insoluble in dilute acids, such as the ferric or copper salt, by simply heating an alkaline deutazophosphate with some acid solution of the metal. In this way azophosphoric acid may be obtained from chlorophosphuret of nitrogen, anhydrous phosphoric acid, or oxychloride of phosphorus.

## ANALYTICAL RESULTS.

In approaching the question of the true composition of these bodies, it seemed desirable to repeat the crucial experiment, which appeared to show that, in the conversion of a deutazophosphate into an azophosphate, only two-thirds of the phosphorus was capable of passing into the new compound. This was tried as follows:—

·483 grm. chlorophosphuret, dissolved in alcohol, decomposed by ammonia, the solution mixed with ferric sulphate, acidified, and boiled, yielded ·518 grm. azophosphate of iron, dried at 100° C.

On the one theory ·483 grm. $P_3N_2Cl_5$ contain ·150 grm. P,
and ·518 grm. $Fe_2O_3,P_2NO_5,4HO$, contain ·139 grm. P;
and on the other theory ·483 grm. $PNCl_2$, contain ·129 grm. P,
and ·518 grm. $Fe_2P_2NH_2\Theta_6,H_2\Theta$ contain ·129 grm. P.

It would appear therefore that when the experiment is made with every precaution to ensure the complete conversion of the one body into the other, the whole of the phosphorus passes from the chlorophosphuret, through the deutazophosphate, into the azophosphate—a result fatal to one at least of the formulæ originally assigned to these bodies, and rendering imperative a revision of the analyses.

*Chlorophosphuret of Nitrogen.*—The difficulty formerly experienced in analysing chlorophosphuret of nitrogen consisted in the estimation of the nitrogen and phosphorus, but we have found a process which is easy and gives satisfactory results. The crystals dried at 100° C. are dissolved in alcohol, and treated with a very strong aqueous solution of ammonia; this produces chloride and deutazophosphate of ammonium; the solution is evaporated to dryness and redissolved in water; the chlorine may then be thrown down by a silver salt in the presence of nitric acid. After separating the excess of silver by hydrochloric acid, the solution is boiled for some hours, to convert the deutazophosphoric acid into tribasic phosphoric acid, which may be determined in the usual manner. It is necessary to assure oneself that the phosphoric acid has been entirely converted into the tribasic condition. To determine the nitrogen, the alcoholic solution is decomposed by pure soda, the solution boiled with excess of hydrochloric acid, and the ammonia precipitated as platinum-salt.

I.—·9255 grm. gave 2·2715 grm. AgCl, and ·8715 grm. $Mg_4P_2\Theta_7$.
II.—·603 grm. gave 1·4905 grm. AgCl, and ·5605 grm. $Mg_4P_2\Theta_7$.
III.—·441 grm. gave 1·088 grm. AgCl, and ·418 grm. $Mg_4P_2\Theta_7$.
IV.—·4866 grm. gave ·9065 grm. $PtCl_2NH_4Cl$.

The following are the percentage results compared with the rival formulæ $P_3N_2Cl_5$ and $PNCl_2$. It will be seen that they agree best with that of Laurent:—

| | Calculated. | | Found. | | | |
|---|---|---|---|---|---|---|
| | $P_3N_2Cl_5$ | $PNCl_2$ | I. | II. | III. | IV. |
| Phosphorus | 31·15 | 26·72 | 26·29 | 25·96 | 26·44 | |
| Nitrogen | 9·38 | 12·07 | — | — | — | 11·73 |
| Chlorine | 59·46 | 61·21 | 60·72 | 61·15 | 61·02 | |
| | 100·00 | 100·00 | | | | |

The formula, or atomic weight, of this body cannot be controlled by the analysis of a compound, as none are known to exist, but two determinations of its vapour-density gave the following results:—

| | I. | II. |
|---|---|---|
| Difference between weight of air and vapour .. .................... | ·633 grm. | ·5722 grm. |
| Temperature of balance case........ | 8°C | 11·C |
| Temperature of sealing............ | 299°C | 306°C |
| Capacity of globe ................ | 101·7 c.c. | 94·02 c.c. |
| Residual air .................... | 1·7 c.c. | ·6 c.c. |
| Calculated density of vapour ...... | 12·33 | 12·09 |

Mean 12·21.

This vapour-density is very high, and in order to make an atom of chlorophosphuret of nitrogen occupy the same space as one of water $H_2\Theta$, it is necessary to triple Laurent's formula, and $P_3N_3Cl_6$ would give a vapour-density of 12·10, almost exactly that found by experiment.

*Deutazophosphoric acid.*—In the previous paper, the formula of this acid was deduced inferentially rather than from the analyses of the deutazophosphates of barium and ammonium, which alone were examined quantitatively; but we thought it desirable to prepare some salt of this acid, if possible, and analyse it. Many attempts were made, but the only success was with the silver-salt prepared in the following manner:—Chlorophosphuret of nitrogen was decomposed by alcohol and ammonia, and from the neutral solution the mixed chloride and deutazophosphate of silver were precipitated by nitrate of silver in the cold, then collected, and washed with as little cold water as possible, as the deutazophosphate slightly soluble. It was dried in vacuo, and a weighed portion boiled with dilute nitric acid, which dissolved the deutazophosphate and left the chloride; this of course had to be subtracted from the original weight; from the solution hydrochloric acid separates the silver, and after boiling for some hours converts the acid into ammonia and tribasic phosphoric acid.

I.—1·203 grm. of mixed silver salts yielded ·8345 grm. original AgCl, ·264 grm. precipitated AgCl, and ·210 grm. $Mg_4P_2O_7$.
II.—·302 grm. deutazophosphate gave ·218 grm. AgCl, and ·170 grm. $Mg_4P_2O_7$.
III.—·2666 grm. gave ·300 grm. $PtCl_2NH_4Cl$.
IV.—·335 grm. gave ·241 AgCl, and ·187 grm. $Mg_4P_2O_7$.
V.—·3132 grm. gave ·3435 grm. $PtCl_2NH_4Cl$.
VI.—·464 grm. ignited per se, the water collected by means of sticks of potash, and the ammonia by hydrochloric acid, yielded ·007 grm. $H_2O$ and ·2545 grm. $PtCl_2NH_4Cl$.

The silver-salt of this acid prepared from oxychloride of phosphorus gave as follows:—

VII.—·543 grm. yielded ·404 grm. AgCl, and ·266 grm. $Mg_4P_2O_7$.
VIII.—·3405 grm. gave ·2475 grm. AgCl, and ·417 grm. $PtCl_2NH_4Cl$.

The following are the percentage results, and they agree sufficiently well with the formula $Ag_2P_2N_2H_4O_5$:—

| | Calculated. | | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
|---|---|---|---|---|---|---|---|---|---|---|
| $Ag_2$ | 216 | 55·38 | 53·94 | 54·33 | — | 54·12 | — | — | 55·98 | 54·7 |
| $P_2$ | 62 | 15·89 | 15·91 | 15 72 | — | 15 59 | — | — | 15 50 | — |
| $N_2$ | 28 | 7·18 | — | — | 7·05 | — | 6·87 | — | — | 7 67 |
| $H_4$ | 4 | 1·03 | — | — | — | — | — | ·91 | — | — |
| $O_5$ | 80 | 20·52 | — | — | — | — | — | — | — | — |
| | 390 | 100·00 | | | | | | | | |

In experiment VI. the ·2545 grm. of platinum-salt obtained is equivalent to 3·51 per cent. of nitrogen, and shows that when this salt was heated per se, only one-half of its nitrogen was evolved as ammonia.

The silver-salt obtained from anhydrous phosphoric acid treated with ammonia, gave too little nitrogen, and was in fact more or less metaphosphate of silver. Schiff may have been more fortunate in obtaining pure deutazophosphates, or phosphamates, but there is no proof of this in his analyses; for he only determined the metal and the phosphorus, and these are almost the same in percentage amount in a metaphosphate and a "phosphamate." Thus in the barium-salt:—

| | Phosphamate. | Schiff's analysis. | Metaphosphate. |
|---|---|---|---|
| Barium........ | 46·6 | 47·1 | 46·4 |
| Phosphorus .... | 21·3 | 21·2 | 21·2 |

The oxychloride of phosphorus afforded the means of preparing other deutazophosphates.

*Zinc-salt.*—This is a gelatinous precipitate, readily soluble in acids, and to some extent in ammoniacal salts; when dry it forms a white powder.

I.—·456 grm. fused with carbonates of potassium and sodium and a little nitre, yielded ·153 grm. $Zn_2\Theta$, and ·415 grm. $Mg_4P_2\Theta_7$.

II.—·441 grm. gave ·828 grm. $PtCl_2NH_4Cl$.

These are equivalent to the following percentages; agreeing with the formula $Zn_2P_2N_2H_4\Theta_5$:—

| | Calculated. | | I. | II. |
|---|---|---|---|---|
| $Zn_2$ | 65 | 27·20 | 26·84 | — |
| $P_2$ | 62 | 25·94 | 25·41 | — |
| $N_2$ | 28 | 11·72 | — | 11·77 |
| $H_4$ | 4 | 1·67 | — | — |
| $\Theta_5$ | 80 | 33·47 | — | — |
| | 239 | 100·00 | | |

*Barium-salt.*—This also was a gelatinous precipitate which dried to a white earthy powder.

I.—·3995 grm. gave ·2975 grm. $Ba_2S\Theta_4$ and ·57 grm. $PtCl_2NH_4Cl$.

II.—·4395 grm. gave ·329 grm. $Ba_2S\Theta_4$ and ·298 grm. $Mg_4P_2\Theta_7$.

These determinations agree with the formula $Ba_2P_2N_2H_4\Theta_5$.

| | Calculated. | | I. | II. |
|---|---|---|---|---|
| $Ba_2$ | 137·2 | 44·08 | 43·81 | 44·04 |
| $P_2$ | 62·0 | 19·91 | — | 18·94 |
| $N_2$ | 28·0 | 9·00 | 8·94 | — |
| $H_4$ | 4·0 | 1·27 | — | — |
| $\Theta_5$ | 80·0 | 25·74 | — | — |
| | 311·2 | 100·00 | | |

*Azophosphoric Acid.*—There is less difficulty in the preparation of pure azophosphates, for some of the metallic salts form in an acid solution, and are very stable.

The analyses formerly recorded gave results which differed little from those required by Laurent's formula, unless perhaps in the amount of hydrogen, but it was considered desirable to obtain additional determinations by a method similar to that which had been found so successful in the analysis of the compounds already described.

*Ferric-salt.*—This salt was dried at 100° C., but it was found to be difficult to obtain it perfectly dry at that temperature, and it was very hygroscopic. The ferric oxide was separated by a solution of caustic soda, the washed precipitate redissolved in acid, and precipitated again by ammonia, while the soda solution was treated with a large excess of hydrochloric acid, and boiled to convert the azophosphoric acid into phosphoric acid and ammonia. The hydrogen was found to be capable of estimation by the usual process of organic combustion.

I.—·242 grm. azophosphate, prepared from chlorophosphuret of nitrogen, gave ·075 grm. $Fe_4\Theta_3$ and ·2085 grm. $Mg_4P_2\Theta_7$.

II.—·243 grm. gave ·076 grm. $Fe_4\Theta_3$. The solution containing azophosphoric acid was boiled with caustic soda, and the ammonia condensed in hydrochloric acid produced ·2005 grm. $PtCl_2NH_4Cl$; from the residue ·2078 grm. $Mg_4P_2\Theta_7$ was obtained.

III.—·400 grm. gave ·066 grm. $H_2\Theta$.

IV.—·575 grm. gave ·0995 grm. $H_2\Theta$.

V.—·4515 grm., prepared from anhydrous phosphoric acid, gave ·1425 grm. $Fe_4\Theta_3$.

VI.—·4035 grm. of the same gave ·3625 grm. $PtCl_2NH_4Cl$.

VII.—·2375 grm., prepared from oxychloride of phosphorus, gave ·2045 grm. $PtCl_2NH_4Cl$.

VIII.—·450 grm. of the same gave ·1435 grm. $Fe_4\Theta_3$. and ·41 grm. $Mg_4P_2\Theta_7$.

The following are the percentages deduced from these numbers, showing that the salt is of the same composition from whichever compound of phosphorus it was originally prepared, and that the ratio of the iron, phosphorus, and nitrogen was correctly determined before. The formula $Fe_2{}'''P_2NH_2\Theta_6.H_2\Theta$ is sufficiently accordant with the results, if we suppose that the last traces of water were not always removed at 100° C:—

| Calculated. | | | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | Mean of former experiments. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Fe_2$ | 56 | 22·58 | 21·60 | 21·96 | — | — | 22·09 | — | — | 22 32 | 23·83 |
| $P_2$ | 62 | 25·00 | 23·96 | 23·98 | — | — | — | — | — | 25·44 | 25·30 |
| N | 14 | 5·65 | — | 5·16 | — | — | — | 5 63 | 5 40 | — | 5·45 |
| $H_4$ | 4 | 1·61 | — | — | 1 83 | 1 91 | — | — | — | — | 1·87 |
| $\Theta_7$ | 112 | 45·16 | — | — | — | — | — | — | — | — | — |
| | 248 | 100 00 | | | | | | | | | |

Schiff analysed an iron-salt which was unquestionably this one, though he viewed it as the phosphamate (deutazophosphate) of ferrous oxide. The mean of his determinations comes remarkably close to the calculated numbers, viz.:—

| | |
|---|---|
| Iron | 22·51 |
| Phosphorus | 24·95 |
| Hydrogen | 1·63 |

He does not give his determinations of nitrogen, but says, in reference apparently to all the salts analysed by him, that they were considerably too low. His formula in fact requires 11 per cent. His determinations were doubtless more correct than he imagined.

*Copper-salt.*—The copper salt was originally prepared in the same way as the ferric salt, and the former analyses, though not made by our present improved method, are sufficiently accordant with the rectified formula, $Cu_3P_2NH_2\Theta_6.H_2\Theta$.

| Calculated. | | | Mean of former experiments. |
|---|---|---|---|
| $Cu_3$ | 94·8 | 33·05 | 33·85 |
| $P_2$ | 62·0 | 21·62 | — |
| N | 14·0 | 4·88 | 4·72 |
| $H_4$ | 4·0 | 1·40 | 1·94 |
| $\Theta_7$ | 112·0 | 39·05 | — |
| | 286·8 | 100·00 | |

*Zinc-salt.*—When the filtrate from the precipitate of deutazophosphate of zinc, containing the deutazophosphate dissolved by the ammoniacal salts and excess of chloride of zinc, is boiled, it becomes turbid and deposits a white granular powder, which was found to be anhydrous azophosphate of zinc.

I.—·455 grm. gave ·202 grm. $Zn_2\Theta$, and ·363 grm. $Mg_4P_2\Theta_7$.

II.—·4556 grm. gave ·473 grm. $PtCl_2,NH_4Cl$.

These numbers give the following percentages, agreeing with the formula $Zn_3P_2NH_2\Theta_6$ :—

| | Calculated. | | I. | II. |
|---|---|---|---|---|
| $Zn_3$ | 97·5 | 35·91 | 35·63 | — |
| $P_2$ | 62·0 | 22·83 | 22·28 | — |
| N | 14·0 | 5·16 | — | 5·12 |
| $H_2$ | 2·0 | 0·74 | — | — |
| $\Theta_6$ | 96·0 | 35·36 | — | — |
| | 271·5 | 100·00 | | |

*Barium-salt.*—This salt is formed under exactly the same circumstances as the zinc-salt, the deutazophosphate of barium in solution being decomposed at a high temperature by the excess of barium-salt.

It falls as a white granular precipitate readily soluble in hydrochloric or nitric acid, but insoluble in acetic acid. The following analyses show that it is anhydrous, and agree with the formula $Ba_3,P_2NH_2\Theta_6$ :—

I.—·2388 grm. gave ·2185 grm. $Ba_2S\Theta_4$.

II.—·345 grm. gave ·316 grm. $Ba_2S\Theta_4$.

III.—·415 grm. gave ·3815 grm. $Ba_2S\Theta_4$, and ·2435 grm. $Mg_4P_2\Theta_7$.

IV.—·739 grm. gave ·675 grm. $Ba_2S\Theta_4$, and ·429 grm. $PtCl_2NH_4Cl$.

These numbers yield the following percentages :—

| | Calculated. | | I. | II. | III. | IV. |
|---|---|---|---|---|---|---|
| $Ba_3$ | 205·8 | 54·21 | 53·85 | 53·95 | 54·08 | 53·74 |
| $P_2$ | 62·0 | 16·32 | — | — | 16·38 | — |
| N | 14·0 | 3·68 | — | — | — | 3·64 |
| $H_2$ | 2·0 | 0·53 | — | — | — | — |
| $\Theta_6$ | 96·0 | 25·26 | — | — | — | — |
| | 379·8 | 100·00 | | | | |

The salts of barium and silver formerly analysed do not give good results, but this is easily accounted for by their mode of preparation. The iron-salt was decomposed by potash, and from this solution they were prepared by double decomposition; now when a caustic alkali is added to the ferric salt, there seems to be always a slight odour of ammonia produced, showing a partial decomposition of the acid, and a consequent formation of phosphoric acid, which will cause an admixture of more or less phosphate with the azophosphate examined. The same remark applies to the potassium-salt formerly analysed.

Hitherto we have concerned ourselves simply with the ultimate composition of the bodies analysed, and have called them by the names originally given; but we must add a few words on their probable rational composition, though we hope some experiments now in progress will throw additional light on this subject.

No formula can yet be assigned for the formation of chlorophosphuret of nitrogen by the action of ammonia, or its compounds, on pentachloride of phosphorus. It seems to be in all cases a secondary product. It would be idle to speculate as yet on how the compound molecule $P_3N_3Cl_6$ is built up, and its old name, chlorophosphuret of nitrogen, may be as good as any other.

The names azophosphoric and deutazophosphoric acid have this significance, that the one acid contains a portion of nitrogen as well as phosphorus and oxygen, and the other a second portion, but it seems preferable to adopt the names given by Laurent, who first divined their true composition. These are *pyrophosphamic* and *pyrophosphodiamic acids*.

The reactions by which pyrophosphodiamic acid is produced according to the methods above described, are as follows:—

$$2P_3N_3Cl_6 + 15H_2\Theta = 3(P_2N_2H_6\Theta_5) + 12HCl.$$

$$P_2\Theta_5 + 2NH_3 = P_2N_2H_6\Theta_5.$$

$$2PCl_3\Theta + 2NH_3 + 3H_2\Theta = P_2N_2H_6\Theta_5 + 6HCl.$$

and the reaction by which pyrophosphamic acid may be derived from it, will be as follows:—

$$P_2N_2H_6\Theta_5 + H_2\Theta = P_2NH_5\Theta_6 + NH_3.$$

or in actual experiment—

$$P_2N_2H_4M_2\Theta_5 + MCl + H_2\Theta = P_2NH_2M_3\Theta_6 + NH_4Cl.$$

## XXVIII.—*On a New Method of Gas-analysis.*

### By A. W. Williamson, F.R.S., and W. J. Russell, Ph.D.

On a former occasion* we described a simple and accurate process for the measurement of gases, and its application to gas-analysis. The especial advantages of the process are that a smaller number of observations are necessary to ascertain the true volume of a given amount of gas, and that the calculations necessary to deduce, from the observed volume, the bulk it occupies at the standard temperature and pressure, are entirely eliminated. The process thus renders the measurement of a gas more expeditious, and in making it a simpler operation, renders it more accurate, by diminishing the chances of error.

The principle on which the process depends is that of using, as a standard of comparison, a constant quantity of air, which is always brought to the same volume. This is effected by marking off, once for all, on the tube containing the air, the height at which the mercury stands; then the effect which any rise or fall of either the barometer or thermometer would produce on the bulk of the air, may be exactly counteracted by raising or lowering the tube in the mercury-trough until the mercury again comes to the mark. The gas in the eudiometer has to be brought to exactly the same tension as that of the standard volume of air. This is done by placing the two tubes side by side, and raising or lowering the eudiometer until the column of mercury within it is of the same height as that which is required to bring the standard quantity of air to the original volume. In the communication before alluded to, we described a convenient form of apparatus for measuring gases by this means, and showed its application to the process of gas-analysis described by Bunsen. Experience having confirmed our views with regard to the advantages of this method of measuring gases, we were naturally led to attempt founding upon it a more rapid method of executing analyses.

The forms of apparatus invented by Regnault and Frankland have proved to how great an extent the time required for making an analysis may be diminished by surrounding the tube containing the gas with water instead of air, and by using the reagents in a liquid form; nevertheless, neither of those methods, as is well known, has come into general use. This, we believe, arises mainly from the apparatus being of too delicate and fragile a nature. In order to stand ordinary laboratory use, an apparatus of this kind must, we are convinced, be without stop-cocks or other delicate mechanism. It must also be constructed of such a form as not easily to be broken, and these requisites must be obtained without in any way diminishing the accuracy of the process. To construct an apparatus having these qualifications was far from an easy task, and it is only after considerable labour and numerous experiments that we have been able satisfactorily to accomplish this task. We will not lengthen this communication by describing the different forms of apparatus we have from time to time constructed, and the modifications which they have undergone, but proceed at once to the description of the apparatus in its last and most perfect form.

---

* Proceedings of the Royal Society, vol. ix, p. 218.

The tube containing the standard quantity of air we term the pressure-tube. It is represented in Fig. 1. The wide part of the tube is about 7 in. long, and ¾ in diameter; in fact, it should be a piece of tubing similar to that of which the eudiometer is constructed. The narrow part of the tube is 17 in. long, and ⅜ in diameter.

The pressure-tube is carried by a steel rod, 30 in. long, and ⅜ in diameter, at the end of which is a clamp, consisting of two straight bars, ½ in. wide, ⅛ thick, which extend down the whole length of the wide part of the pressure-tube. Two flexible steel rings are fastened, one near the top of these two bars, the other at the bottom. They are let into and firmly fixed to one bar, and by means of a screw passing through the other bar, the two ends of the ring can be brought together and held securely (Fig. 1). By introducing a little india-rubber padding between these rings and the tube, then screwing the rings tight, the pressure-tube is held with great firmness, and is kept in the same straight line as the rod. Firmly fastened to one of the bars forming this clamp are two other pieces of metal, $l$ $m$, at right angles to it, passing across the back of the tube (Fig. 1). They are 1⅞ in. long, the upper part ⅛ thick, but narrowing gradually, so that the lower edge has only the thickness of a very blunt knife. These two cross pieces serve as marks indicating exactly where the mercury must stand in the tube for the contained air always to have the same volume. We use two marks, in order that when operating with only a small amount of gas, it may be considerably expanded, but that when using a large amount of gas, it need not be expanded to the same extent. The height of the mercury in the pressure-tube is altered by raising or lowering the rod in the clamp; but the final adjustment, the raising or lowering of the mercury, so that the meniscus *exactly* touches the lower edge of the cross-piece, is performed very simply and accurately by altering the level of the mercury in the trough. This is done by screwing up or down a piece of large glass tube, which is in the further end of the trough. We shall allude again to this piece of apparatus when describing the analysis of a gas. It will be seen from what follows that it is absolutely necessary that the steel rod carrying the pressure-tube be perfectly straight, and in order that it may move when raised or lowered in the clamp (Fig. 1), always in one plane, it passes through a tube, which clasps it very accurately, and is six inches long; in fact, the tube is made to act like a spring on the rod by having two slits cut in each end of it. The rod, when greased, slips easily through the tube, but is held firmly by it. If, however, the weight of mercury in the pressure-tube should be too great for this spring to hold, the screw, *n*, is used, which, by pressing against the rod, securely holds it at any point. The whole clamp carrying the pressure-tube slides on one of the long, stout rods passing through the table. A groove is cut in the top of the rod for the screw to move in. The object of this is to retain the clamp always in the same vertical plane. To render the pressure-tube ready for use, a very small drop of water is placed at the closed end, and mercury poured in until only a small quantity of air remains. The tube is then inverted in the mercury-trough, and more air let in, a few bubbles at a time, until when the pressure-tube is brought to its proper position, the mercury within stands near the upper marker.

The tube containing the gas to be analysed is an ordinary Bunsen's eudiometer. It is held and moved up and down in the same kind of way as the pressure-tube. The only difference is that the clamp on the eudiometer is very much shorter than the one on the pressure-tube, its length being only 3 inches. It is constructed in the same way, only without the two horizontal pieces at the back.

There is, however, an essential difference in the upper clamp through which the steel rod passes; to this is attached a simple apparatus for raising or lowering the eudiometer through small distances. It is similar to the fine adjustment we described in our former paper on the measurement of gases. Fig. 2 represents

FIG. 2

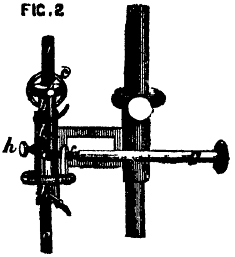


FIG. 3

FIG. 4

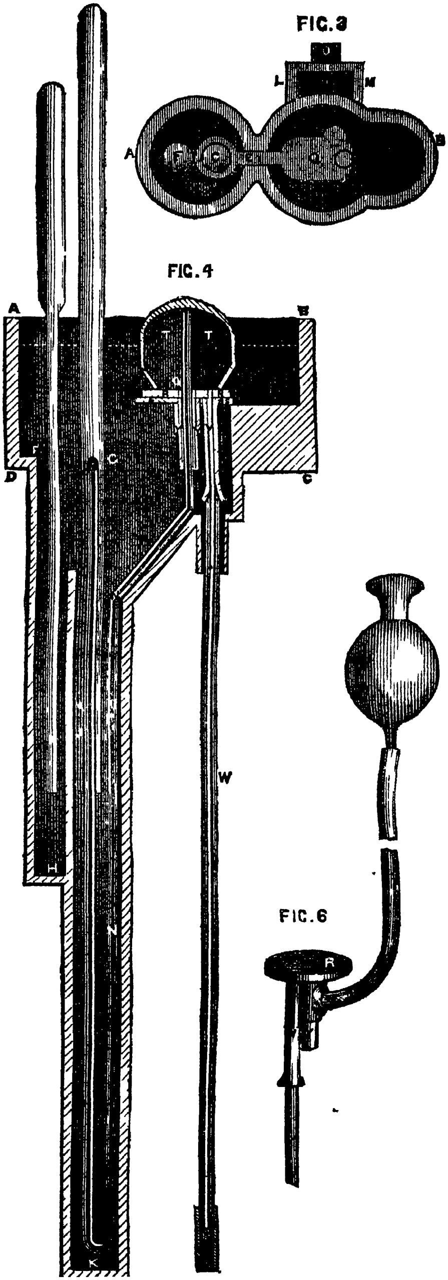


FIG. 1

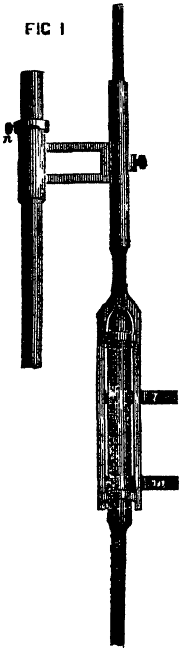


FIG. 5

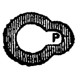


FIG. 7

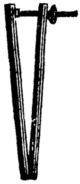
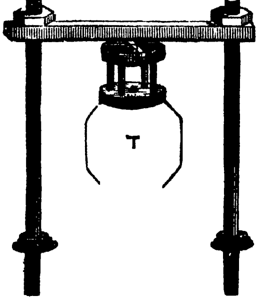


FIG. 6

FIG. 8



this clamp; *a* is the steel rod clamped to the eudiometer; this passes through a stout tube, *b*, and can be firmly attached to it by a screw passing through the top of it, which is thickened for this purpose; the milled head of the screw is seen at *c*. The length of this tube is four inches. Again, this tube is within a second tube, *d*, which is fixed by the bars, *e*, to the tube sliding over the thick rod fastened to the table. The fine adjustment is then effected in this way: a piece of cat-gut which is fastened to the end of the first tube, *b*, is wound round the axis, *f*, and passes through a hole in the centre of it. The handle, *g*, is attached to this axis, so that when it is turned round, one half of the cat-gut unwinds, while the other half winds round the axis, and draws the tube either up or down. *h* is a friction-screw moving up and down in an opening cut in the exterior tube, and is screwed into the inside tube *b*. On tightening this screw, it presses more strongly against the outside tube, thus increasing the friction with which the inside tube moves. This arrangement is necessary as it might often happen when the eudiometer was high out of the trough and nearly full of mercury, that the weight of it was sufficient to unwind the cat-gut on the axis *f*, and cause the tube *b* to fall to its lowest position.

The general form of the mercury-trough, which is made of gutta-percha, is seen in Fig. 3, and Fig. 4 is a section of it through A B. The same letters apply to the same parts as seen in both figs. The sizes given are all inside measurement. The length from A to B is $9\frac{1}{2}$ inches. The thickness of the gutta-percha sides is $\frac{1}{2}$ inch, and their height, as seen at B C and A D, Fig. 4, 5 inches. The left-hand part of the trough, A E, is $3\frac{3}{8}$ inches in diameter and 5 inches deep. F represents the position of the pressure-tube well, which is attached to the bottom of the trough, and G that of the well for the eudiometer. In Fig. 4, F H and G K represent these wells. The former is 15 inches deep and 1 inch in diameter, the latter is 29 inches deep, and for the first 3 inches after it leaves the trough it is $1\frac{9}{16}$th inches in diameter; the lower part of it has the form shown in Fig. 5, the circular part being $1\frac{1}{16}$th inches diameter, and the projecting part $\frac{1}{2}$ inch wide and $\frac{1}{2}$ inch long.

In the right-hand portion of the trough, from E to B (Fig. 3), the greater part of it is solid gutta-percha to a height of 2 inches from the bottom, as seen at B C, Fig. 4. The oblong figure in the middle shows the hole which is made there, and the canal joining what may be called the two troughs. L M is a small additional trough of the same height as the large one.

On referring to the sectional drawing, Fig. 4, the position and arrangement for the movements of the pressure-tube and eudiometer will be easily seen. To the upper part of each of these tubes the clamps before described are screwed, and the steel rods attached pass through and can be held by other clamps fastened to the thick iron rods passing through the table. Into this round part of the trough fits a glass cylinder, about 27 inches high, which is to be filled with water when the apparatus is in use. The cylinder is supported near the top by a ring fastened to one of the iron rods passing through the table, and the mercury in the trough prevents the escape of the water. The cylinder can thus be put on or taken off with great readiness. When the apparatus is in use, the mercury outside the cylinder stands at a height of about 1 inch from the top of the trough. In the method of analysis adopted by Bunsen, the reagents are introduced into the eudiometer. This procedure necessitates the use of only solid reagents, which can absorb the gases but slowly, and besides introducing a small error, namely, that of the gas always adhering to the surface of the reagent, it has the inconvenience, even with the greatest care, of dirtying the inside of the tube, and thus often rendering the reading off of the bulk of gas unsatisfactory. It is quite obvious that to remove these objections, a separate vessel must be used, into which the gas must be passed when the absorption of any of its constituents has to be effected. This is the laboratory tube of Regnault and Frankland. The form of apparatus best suited for this transference of gas from the one tube to the other, is a point which has engaged much of our attention, and after making many experiments on the subject, we have adopted a process which is exceedingly satisfactory. By the means we are about to describe, the passage of the gas from the one tube to the other is complete, and easily effected; the apparatus is not fragile; and there is no stopcock or other source of leakage. Fig. 4 shows how this transference is effected. Down the centre of the eudiometer-well, a glass-tube, N, of about $\frac{3}{8}$ in. diameter and very small bore, passes; it is bent round at the bottom, curving up in the small addition to the well, P (Fig. 5). When within about 5 inches of the trough, the tube, N, bends, as shown in the figure, but afterwards, again becoming straight, rises vertically into the right-hand part of the trough in the centre, Q (Figs. 3 and 4). Over this end of the tube is passed a vulcanised india-rubber pad with a short tube attached to it. This is shown in Fig. 6, and a section of it at R and Y (Fig. 4). The lower part of the india-rubber tube, Y, is bound with wire tightly on to the glass tube, N, so that the tube projects 3 inches above the top of the circular pad, which is 3 inches in diameter and ¼ inch thick. It rests on an iron plate, S, which has a hole in the centre for the tube to pass through. This round pad and iron plate are supported by the solid gutta-percha round the inside of the right-hand portion of the trough. The inside line, Fig. 3, shows how far it extends. The object of the india-rubber pad is to afford an elastic surface for pressing the laboratory-tube upon. The laboratory-tube, or rather laboratory-vessel, we use, is shown in section at T, Fig. 4; it is round and made of rather thick glass. The height of it is 3 inches, so that the syphon-tube, N, reaches exactly to the top of it. The end of the tube should be rounded, so that the middle part is higher than the outside. The laboratory-vessel is pressed down on the caoutchouc pad by means of a flat iron bar passing over the top of it. On each side of the trough there is an iron rod fastened into the table; a hole in one end of the flat bar allows it to pass over one of the rods; and a slot in the other end admits of its being brought so far, that the other rod is also in the centre of the flat bar. A screw is turned on the top of the rods, so that by means of a large nut, the bar may be pressed with very considerable force down on the top of the laboratory-vessel. Instead, however, of the bar pressing directly on the top of the glass, it is better to have a small round iron frame roughly fitting on it, and having on the upper side a wedge-shaped piece of iron, on the thin edge of which the bar before described presses; by this means the pressure is more equally distributed over the whole of the laboratory-vessel. Fig. 8 represents this arrangement.

This laboratory vessel being thus held firmly, we can first expel the air from it by allowing mercury to flow into it through a tube connected with a reservoir of mercury at the height of about 3½ feet above it. This tube and reservoir are seen in Fig. 6; the tube forms part of the caoutchouc pad, and enters the wide part of the tube, Y, at right angles. When the pad is in its position in the trough, it passes through a hole in the side, and then through the small supplementary trough L M (Fig. 3), passing out along the gutta-percha tube U. A short piece of caoutchouc tubing slipped on and bound to both these tubes serves to prevent the escape of the mercury from the trough. The end of this tube is fastened to the vessel, which forms the mercury reservoir. The reservoir is fixed to a wall, or other convenient support, above the trough. The use of the supplementary well, L M (Fig. 3), is to contain a clamp, by which the flow of mercury from the reservoir can be regulated. This clamp is of very simple construction, and is shown in Fig. 7. It is placed in the trough, L M (Fig. 3), before passing the long tube through, so that the tube has to pass between the steel bars. After screwing the nut to a proper position on the rod, we can allow the mercury to flow from the reservoir, simply by raising the rod out of the slot, and allowing the bars to separate, and stop it by again bringing them together and replacing the rod in the slot. By this means we can very conveniently fill the laboratory vessel. The mercury flowing in at the bottom drives the air before it, and causes it to escape through the syphon tube, N (Fig. 4), and the mercury rising gradually to the highest part of the laboratory vessel, expels the last particle of air from it, and then fills the syphon-tube. In this way, the air is expelled at the commencement of an analysis from the laboratory vessel, and a gas, after it has been treated with any reagent, is returned to the eudiometer for measurement. The reverse operation, the drawing the gas out of the eudiometer into the laboratory vessel, is effected by forming a vacuum in this vessel. To accomplish this, there is a small caoutchouc tube, V (Fig. 6), and V (Fig. 4), which is fastened to, or rather forms part of the pad, R. The diameter of this tube is $\frac{1}{8}$ in. It passes through the pad at a distance of $\frac{3}{8}$ in. from the large central tube. The length of the latter tube is 4 in. It should be made of the best vulcanized india-rubber, and be from $\frac{3}{8}$ to $\frac{1}{2}$ in. in diameter. To the end of the central tube is fastened a piece of thick barometer tubing. The joining is best made by grinding the end of the barometer-tube to a conical form, so that it may be forced up the bore of the caoutchouc tube. Before doing this, melted gutta-percha should be dropped on the end of the glass tube, and after binding the tube on as firmly as possible with iron wire, more gutta-percha may be melted round the end of it, so as to render the joint as perfect as possible. The united length of these two tubes should be about 30 in. The flow of mercury through the tubes is regulated by the following contrivance: at the lower end of the glass tube, a short piece of thick caoutchouc tube is bound firmly on and extends about 1½ in. beyond the end of the glass tube. A clamp for regulating the flow of mercury from the reservoir, similar in principle to the one before mentioned, passes across this piece of tubing, and, by tightly compressing it, prevents any mercury from passing through. It would, however, to say the least of it, be an exceedingly inconvenient arrangement if it were necessary for the operator to stoop down every time it was required to open or close this clamp. To avoid this, we use a strong pair of crucible tongs for a clamp. The only addition they require is a rod with a screw and nut fastened to one arm, and a slot made in the other, an arrangement precisely similar to that used with the other clamp (Fig. 7). The flexible tube is placed between the jaws of the tongs meant to clasp the crucible, and by opening or closing the other ends, we regulate the flow of the mercury. The tongs must, of course, be firmly held in one position, so that no strain shall come upon the suction-tube. This is easily done by binding them to a support fixed in the floor. We have now all that is required for effecting the transfer of the gas between the eudiometer and the laboratory vessel. By opening the clamp compressing the tube from the reservoir, and retaining the clamp at the bottom of the suction-tube closed, the gas is forced out of the laboratory vessel into the eudiometer; and by depressing the eudiometer until the top of it touches the end of the syphon-tube, and then opening the clamp at the end of the suction tube, the gas is forced along the syphon into the laboratory vessel. The end of the syphon-tube, which is within the eudiometer, should be rounded as shown in Fig. 4; every particle of the gas can then be withdrawn from the tube.

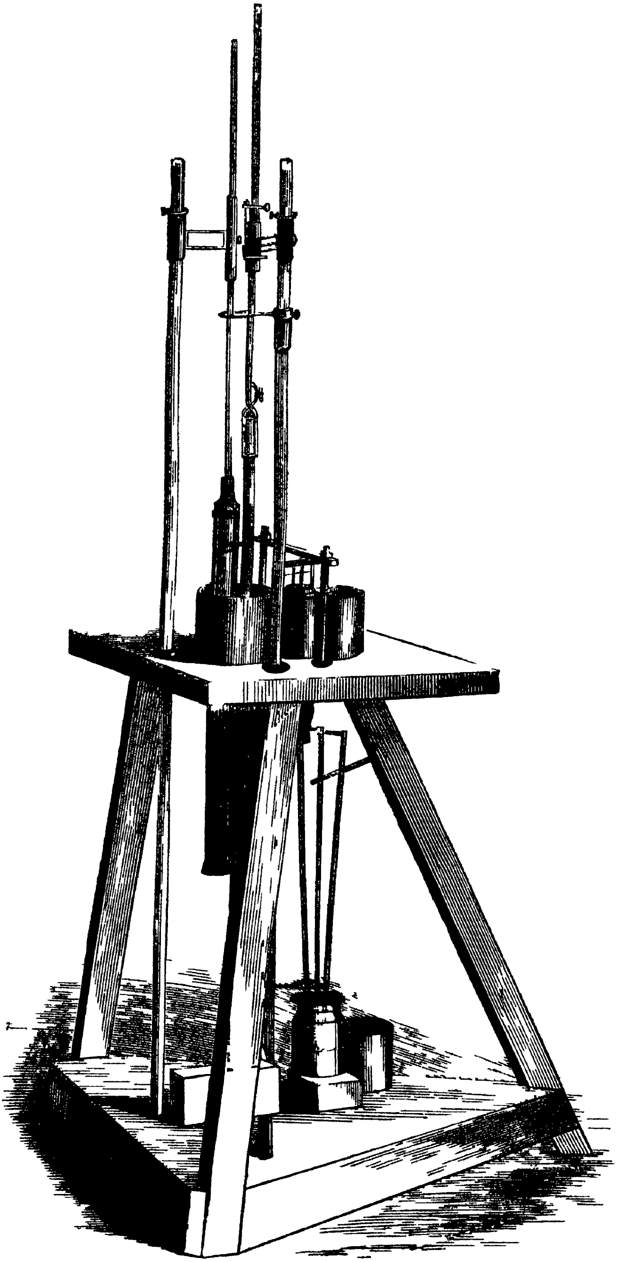
It will readily be seen that this way of filling the eudiometer with mercury is not only simple, but accomplishes the end very satisfactorily; for the air being drawn out from the top of the eudiometer, the mercury rises gradually and regularly, the consequence of which is that no bubbles of air remain adhering to the tube, as they are apt to do when it is filled in the ordinary way. Owing to the elasticity of the syphon-tube, and the upward pressure of the mercury, there is no fear of injuring the eudiometer by pressing it down till the syphon-tube touches the top of it. In order that no bubble of gas may remain adhering to the syphon-tube when the eudiometer is raised, the syphon should be struck once or twice with the end of the eudiometer as it is being lifted up.

While engaged in working out and perfecting this method of transfer of the gas, we have observed several interesting and important facts, which may be briefly mentioned. First, with regard to the imperfection of the joint made by pressing the laboratory vessel down upon the caoutchouc pad. It will be evident that by means of the screws on the rods, and the large nuts, the laboratory vessel can be pressed down with very considerable force. Besides this, the vessel is surrounded, both inside and out, with mercury to a height of one or two inches, but these precautions are not sufficient to prevent air passing into the laboratory vessel, when a vacuum is formed there. In the experiments made to test whether the vacuum remained perfect, or what amount of leakage took place, the flow of mercury through the syphon-tube was prevented by slipping an india-rubber cap over the end of the syphon, the eudiometer, of course, being removed. By this means it could be ascertained whether any leakage of air occurred after several hours, and even after several days. The mere pressing, however strongly, of the laboratory vessel down upon the pad, and surrounding it with mercury, were insufficient to retain a vacuum; in fact, the air can then enter with considerable rapidity, and is seen to bubble up into the laboratory vessel. The amount of leakage under these circumstances far exceeded what we had anticipated. It evidently arises from the want of contact between the mercury and the glass. A layer of air remains adhering to the glass both inside and out. When it is plunged into the mercury, there is thus a continuous chain of particles of air extending from the vacuum to the level of the mercury outside. The pressing of the vessel on the pad does not produce sufficiently close contact between the glass and caoutchouc to prevent the gradual movement of this layer of air, so that as the particles at one end of it pass up into the vacuum, others are drawn in from the surrounding air, and pass gradually along. By a very simple proceeding, we are, however, able to prevent any appreciable error from leakage arising in this way; for it is only necessary to moisten the surface of the pad with water, or a dilute solution of corrosive sublimate, before covering it with mercury, and to fill with water the small hollow round the laboratory vessel produced by the expulsion of the mercury by the glass. When these precautions are taken, and other sources of error to which we shall immediately allude are eliminated, we are able to retain in the laboratory vessel an all but perfect vacuum; a vacuum, it is believed, far exceeding that obtained by any other means of this kind. In fact, if a vacuum be retained for 24 hours in the laboratory vessel, it will be found that the air which has entered, when reduced to atmospheric pressure, does not occupy a space much larger than that of a large pin's head; and it is probable that this small bubble of air has diffused through the water into the vacuum.

For some time after this method of passing the gas between the laboratory vessel and eudiometer as first adopted, we used the flexible tube and reservoir, both for increasing and diminishing the pressure on the laboratory vessel. To do this, it was only necessary to raise and lower the reservoir, which was easily done by means of a cord passing over a pulley; this would have rendered unnecessary the second or glass tube connected with the pad, and there would have been no occasion for the transfer of mercury from one vessel to another. We were, however, obliged to abandon this method, after making numerous experiments on the subject, for the simple reason that it was impossible to obtain any flexible tube perfectly air-tight. Tubes of several kinds were made on purpose for these experiments; some were made with a small bore and composed of three or four layers of the best india-rubber, very carefully joined, so as to form one thick tube, which was slightly vulcanised. Mr. Siemens was good enough to make us a tube of non-vulcanised india-rubber, the joinings in which were united by his machine. Painting the tubes over with a solution of india-rubber or gutta-percha in benzol, while a vacuum existed in the laboratory vessel, was tried, but without success. With by far the greater number of the tubes used, the amount of leakage was very small, and when the apparatus is in use, the vacuum, or a near approach to it, instead of being retained for many hours, as was the case in these experiments, only continues for a very few seconds; still as the small quantities of air thus drawn in might accumulate in the tube, and then rise into the laboratory-vessel, we considered it a sufficient reason for abandoning this plan for varying the pressure. Several methods were tried in which an intermediate vessel was used for collecting any air sucked into the tube; but this addition rendered the apparatus more complicated, and did not altogether give satisfactory results. With the glass tube adopted there is perfect freedom from leakage, and it adds but little to the size of the apparatus or to the trouble in manipulating. Fig. 9 represents a general view of the apparatus.

We now proceed to describe the method of using the apparatus and the precautions to be attended to. When filling the trough with mercury, care should be taken that air does not remain

Fig 9.



lodged under the caoutchouc pad; also, that the pad and neighbouring parts are well wetted, so as to prevent air being sucked in in the manner before described; in fact, it is best to fill the trough first with water and then pour in the mercury; this process also wets thoroughly the end of the small caoutchouc tube (Fig. 6), into which the glass one is fastened; if this is not attended to, a leakage might take place here in the same manner as at the laboratory vessel. The flexible tube connected with the mercury reservoir should also be well wetted before filling with mercury, and a little water always kept on the mercury in the reservoir; for if this is not done and the tube become dry, air can pass along it, and, in time, may find its way into the laboratory vessel. The suction-tube is easily filled by first filling the laboratory vessel, and then opening the clamp at the bottom of the glass tube, and the clamp on the reservoir tube may also be opened at the same time if necessary to drive the last bubbles of air out. A wide-mouthed bottle, or any other convenient vessel of that kind may be used to catch the mercury as it flows from the suction-tube, the end of which should always be kept below the surface of mercury. A convenient arrangement is to have a Wurtemberg syphon, one limb of which dips into this bottle, so as to retain the proper amount of mercury in it, and the other limb passes into a second vessel. The mercury flowing down the suction-tube runs first into the bottle and then along the syphon into the other vessel. When this mercury is again required, the vessel containing it is removed from below the syphon and the mercury poured out of it into the upper reservoir. When the trough and tubes are properly filled, the mercury should be dried, the end of the syphon-tube closed by the caoutchouc-cap, and a vacuum formed in the laboratory vessel. This should be left for some hours, then the cap removed from the end of the syphon-tube, and the laboratory vessel filled with mercury. This expels through the syphon-tube all the air or water which has been sucked in. It may be necessary to repeat this process two or three times, in fact until, after leaving the vacuum for twelve or fourteen hours, it is found that nothing more than an exceedingly small bubble of air has entered. The apparatus should always be put to this very severe test before using it. When not in use it is well to keep the surface of the mercury wet.

The telescope, or rather magnifying-glass, used in observing the height of the mercury consists of a single convex glass set in a tube. The opening at which the eye is placed is very small;

this avoids any appreciable error from parallax. Within the tube are two fine platinum wires crossing in the centre at right angles. The straight brass rod about 2 feet 3 inches long carrying the telescope, is fixed into a heavy stand provided with three levelling-screws; this rests on the table which supports the mercury trough. The telescope is fastened to a short arm fixed to a brass tube 6 inches long, which clasps the vertical rod, and to prevent this tube having any lateral movement, the ends of it have a slit cut in them, so that they act as a spring, an arrangement similar to that used with the pressure-tube and before described. A small ring provided with a screw passing through it also slides on the rod, so that it can be fixed to the rod at any point. The tube carrying the telescope rests on this ring, and is free to move in a horizontal plane. We can thus read off the height of the mercury in the eudiometer and pressure-tube. These tubes being close together, the angle through which the telescope has to move is small. The focal length of the magnifier used should be about 6 or 8 inches.

Let us, now, suppose a gas introduced into the eudiometer, and the cylinder filled with water; the volume of the gas is read off in the following way: The pressure-tube is raised or lowered by means of the clamp and rod attached to it, so as to bring the mercury in it about to the level of the lower edge of the horizontal marker which is to be used; next the eudiometer is adjusted in the same kind of way, so that the column of mercury in it is about the same height as that in the pressure-tube; the telescope is then adjusted to the proper height, and directed to the mark behind the pressure-tube, the mercury raised or lowered, as the case may be, by giving a screw movement either up or down to the glass tube, dipping into the mercury at the end of the trough. This tube is simply held by a clamp fastened into the table, and moves in it with considerable friction. By this means, while looking through the telescope, the mercury in the pressure-tube may, with the greatest accuracy, be made exactly to touch the bottom of the horizontal mark, which thus forms a tangent to the meniscus. The readings off are rendered much more certain, and are accomplished with much greater ease, if a screen of silver paper is placed at a short distance behind the apparatus, and in front of the source of light, which may be either an Argand-burner (the most convenient) or a window. The paper produces a diffused light over the whole apparatus, which renders the different parts, as seen through the telescope, very distinct. The two markers are made $\frac{3}{8}$ in. deep, so that they throw a shadow on the meniscus of mercury, thus rendering it quite black. The illuminated silver paper forms the back-ground, and gives the greatest possible distinctness to it. A slight touch now moves the telescope in the same horizontal plane, so that the eudiometer comes into view. The two markers, *l* and *m*, Fig. 1, it will be seen, project beyond the pressure-tube, and reach to about half-way across the eudiometer, and the next operation is to bring the mercury meniscus in the eudiometer to such a height that it also exactly touches the lower edge of the marker. This raising or lowering of the mercury is effected by means of the fine adjustment before described attached to the upper clamp, which holds the eudiometer. The bringing of the mercury to the required height is as easy as in the former case; the only difference is that the marker, extending in this case only half-way across the tube, leaves half of the meniscus illuminated, while the other half behind the marker is quite dark, similar to the meniscus in the pressure-tube. After adjusting the mercury in the eudiometer, so that the marker behind it is a tangent to the highest part of the meniscus, the telescope should again be turned to the pressure-tube, in order to ascertain whether any appreciable alteration of the height of the mercury in it has taken place, by the raising or lowering of the eudiometer; and if so it is readjusted, which is but the work of a moment. The mercury in the eudiometer is again brought to the mark, and the height of the top of the meniscus read off on the graduated scale of the tube. Since the right-hand half of the meniscus has no marker behind it, this is easily done, the diffused light behind rendering the graduation on the eudiometer particularly distinct. If the light behind should be so strong as to render the illuminated half of the meniscus somewhat indistinct, it is brought out with great sharpness by holding between it and the paper screen any opaque body, so as to throw its shadow on the meniscus, but without cutting off the light immediately above the meniscus. It is most convenient if the figures are written on the right-hand side of the scale etched on the tube.

In a former part of this paper, we have described the clamp which holds the rod carrying the pressure-tube, and have dwelt on the necessity of this rod being quite straight. It will now be evident that it is necessary for the accuracy of this method of measuring a gas, that the pressure-tube should move up and down, so that the two markers attached to it always remain in a horizontal direction. The clamp sliding on the pillar passing through the table is always screwed to it exactly at the same place as shown by a mark on the rod. Before using the apparatus, it must be ascertained that the two markers are perfectly horizontal, and that they maintain this position when the pressure-tube is raised or lowered to its fullest extent. The best method of doing this is to place immediately behind one of the markers a small glass vessel, with flat sides, containing mercury; then, on raising or lowering the tube, or by altering the amount of mercury in the vessel, the surface of the mercury may be brought close up to the lower edge of the marker, and by comparing the two throughout their whole length, especially when the distance between them is very small, it is at once seen whether the marker is horizontal. The observation may be made with the telescope, the paper screen and lamp being used. If this test shows the markers not to be horizontal, they are brought into that position by altering the level of the table, which should be a three-legged one. This is done either by screws fixed to the legs, or simply by introducing very thin wedges under the legs.

It will be obvious that there are several advantages in having the lower part of the pressure-tube smaller than the upper part, for it then requires a smaller well to move freely up and down in, and less mercury to fill both tube and well. Care must be taken that the pressure-tube does not at any time touch the sides of this well; for if it did, that would, of course, throw the markers out of their horizontal position. The tube, on being tapped, should always vibrate readily; this shows that it hangs free. Again, by diminishing the amount of mercury in the pressure-tube as much as possible, we diminish the tendency it has to draw the iron pillar which supports it out of the vertical direction. When once properly adjusted, we do not find these markers liable to alter their position. All the readings are made with the gas saturated with moisture. A drop of water is introduced into the eudiometer before filling it with mercury, and enough of it always remains adhering to the tube to saturate the gas, even if the eudiometer has, in the course of an analysis, been filled two or three times with mercury. A very small quantity of water, as before mentioned, is also introduced into the pressure-tube to saturate the standard volume of air. Any alteration in the temperature of the water surrounding the tubes during an analysis will not, as before pointed out, affect the accuracy of the results, provided that both tubes have undergone the same change of temperature. Since they are surrounded by some quantity of water, this condition is easily ensured by thoroughly agitating the water from time to time. This may conveniently be done by means of a wooden stirrer, having the form of a hoe.

To give an idea of the accuracy of this method, we may cite a few consecutive analyses of air freed from carbonic acid:—

*1st Specimen of Air.*

| | | | |
|---|---|---|---|
| Air employed | 202·83 | Oxygen | 21·002 |
| After addition of hydrogen | 363·84 | Nitrogen | 78·998 |
| After explosion | 236·04 | | |
| | | | 100·000 |

| | | | |
|---|---|---|---|
| Air employed | 213·87 | Oxygen | 20·997 |
| After addition of hydrogen | 376·49 | Nitrogen | 79·003 |
| After explosion | 241·77 | | |
| | | | 100·000 |

| | | | |
|---|---|---|---|
| Air employed | 252·42 | Oxygen | 20·991 |
| After addition of hydrogen | 419·58 | Nitrogen | 79·009 |
| After explosion | 260·62 | | |
| | | | 100·000 |

*2nd Specimen of Air.*

| | | | |
|---|---|---|---|
| Air employed | 201·18 | Air employed | 211·10 |
| After addition of hydrogen | 353·34 | After addition of hydrogen | 375·37 |
| After explosion | 226·74 | After explosion | 242·59 |

| | | | |
|---|---|---|---|
| Oxygen | 20·976 | Oxygen | 20·966 |
| Nitrogen | 79·024 | Nitrogen | 79·034 |
| | 100·000 | | 100·000 |

| | | | |
|---|---|---|---|
| Air employed | 194·88 | Air employed | 209·66 |
| After addition of hydrogen | 337·38 | After addition of hydrogen | 375·06 |
| After explosion | 214·83 | After explosion | 243·21 |

| | | | |
|---|---|---|---|
| Oxygen | 20·961 | Oxygen | 20·962 |
| Nitrogen | 79·039 | Nitrogen | 79·038 |
| | 100·000 | | 100·000 |

It will be seen that in these analyses a comparatively small bulk of air was operated on, so that even a small absolute error would have led to a considerable alteration in the per centage composition of the air.

It now only remains for us to describe the method of applying the reagents. These are used generally in a plastic form; for instance, if a gas has to be subjected to the action of caustic potash, more or less of the inside of the laboratory vessel is covered with the reagent, by means of a wire brush. To obtain the potash of the proper degree of consistency, it is fused with a little water in a silver crucible. The small brush, made by binding a number of short pieces of thin iron wire together, is from time to time dipped into it, and the potash adhering to it spread on a piece of glass. The evaporation should be carried on till the trial-drop becomes solid on cooling, but still has a translucent appearance. The lamp is then immediately removed from under the crucible, and the potash is painted on the inside of the laboratory vessel round the middle, but not carried far up the conical part of it. Immediately after this operation is completed, the glass is placed in its position over the syphon-tube, screwed down, and filled with mercury, the eudiometer having, of course, been previously raised out of the well and placed on one side, where it is supported by its clamp. The application of the reagent in this way has several advantages over any other method that has been proposed. If any air should adhere to the surface of the potash, the means exist of entirely removing it. This is done simply by forming a vacuum in the laboratory vessel; the air immediately diffuses into it, and is expelled through the syphon-tube by allowing the mercury to flow into it from the reservoir. After the gas has been in contact with the potash, a vacuum is again formed, and the adhering gas, if any, passed into the eudiometer.

The caustic potash, when painted on in the proper condition, absorbs carbonic acid very rapidly, the absorption of a large amount of carbonic acid being completed in five minutes. The special object of not painting the top of the laboratory vessel with potash, is that in case a little of it should become liquid and float on the mercury, this will attach itself to the glass and not be carried into the syphon-tube. In case, by any accident, potash should be carried into the syphon-tube, it is easy to draw a little water through it, which will, of course, immediately remove it.

The following are two analyses made of a mixture of air and carbonic acid:—

| | |
|---|---|
| Volume of gas taken .. .. | 248·02 |
| After absorption by potash .. | 201·80 |
| After addition of hydrogen .. | 356·80 |
| After explosion .. .. | 231·25 |

| | |
|---|---|
| Volume of gas taken .. .. | 230·63 |
| After absorption by potash .. | 187·56 |
| After addition of hydrogen .. | 331·11 |
| After explosion .. .. | 214·17 |

| | |
|---|---|
| Carbonic acid | 18·64 |
| Oxygen .. | 16·87 |
| Nitrogen .. | 64·49 |
| | 100·00 |

| | |
|---|---|
| Carbonic acid | 18·68 |
| Oxygen .. | 16·90 |
| Nitrogen .. | 64·42 |
| | 100·00 |

For the absorption of oxygen the simplest way of applying pyrogallate of potash, is to prepare the potash in the way before described, and then just before painting it on the laboratory vessel, some pyrogallic acid is added, and the mixture applied by means of the wire-brush.

The fuming sulphuric acid for the absorption of hydrocarbons is best applied by means of a coke ball. The gas is passed over into the laboratory vessel, the bar which presses it down taken off, and the coke ball introduced in the ordinary way; the absorption of the hydrocarbons takes place very rapidly. A potash-ball is afterwards introduced to absorb the acid vapours. As far as the form of this apparatus is concerned, it will be evident there is nothing to prevent the use of solid reagents in all cases if thought desirable.

The following are analyses of mixtures of known quantities of different gases:—

| | |
|---|---|
| Volume of air employed .. .. .. | 182·45 |
| After addition of hydrogen .. .. | 213·84 |
| After addition of carbonic acid .. .. | 257·98 |
| After absorption by potash .. .. | 213·84 |
| After explosion .. .. .. .. | 166·72 |

| | Employed. | Found. |
|---|---|---|
| Carbonic acid .. .. | 17·11 | 17·11 |
| Hydrogen .. .. .. | 12·17 | 12·17 |
| Air .. .. .. .. | 70·72 | 70·72 |
| | 100·00 | 100·00 |

| | |
|---|---|
| Volume of nitrogen employed .. .. | 95·76 |
| After addition of carbonic acid .. .. | 112·14 |
| After addition of oxygen .. .. .. | 132·73 |
| After absorption by potash .. .. .. | 116·27 |
| After addition of hydrogen .. .. .. | 187·70 |
| After explosion .. .. .. .. | 125·88 |

| | Employed. | Found. |
|---|---|---|
| Carbonic acid .. .. | 12·34 | 12·40 |
| Oxygen .. .. .. | 15·51 | 15·52 |
| Nitrogen .. .. .. | 72·15 | 72·08 |
| | 100·00 | 100·00 |

In the last analysis, only a very small quantity of gas was employed, and all the readings, except the one after adding hydrogen, were made by using the lower mark on the pressure-tube, and thus expanding the gas to about double its volume at atmospheric pressure.

Oxygen or hydrogen is introduced into the eudiometer in the same way as in the ordinary process; it is only necessary to use a longer delivery tube, the end of which is introduced within the glass cylinder, by dipping it down the narrow canal joining the two circular troughs.

The best way of introducing into the apparatus the gas to be analysed, will depend upon the form of the vessel which contains it; if it should have a delivery-tube, the gas can at once be bubbled up into the laboratory vessel, which has been previously filled with mercury; if it is contained in a tube, this is passed down over the syphon-tube and the gas sucked out of it into the laboratory vessel. The tube containing the gas is easily brought over the syphon, either by removing the large glass cylinder, or by fastening a stick to the tube, which is done with a couple of caoutchouc rings, dipping the open end of it in a cup of mercury attached to a long rod and thus lowering it into the mercury-trough. A third way is to bubble the gas at once into the eudiometer and then transfer it to the apparatus.*

---

* The complete apparatus may be obtained from Mr. Harrison, 68, Red Lion Street, Clerkenwell Green, London, E.C.

## XXIX.—*On the Action of Baryta upon Suberic and Azelaic Acids.*

By R. S. DALE, Student in the Laboratory of Owens College, Manchester.

ACCORDING to Riche*, the higher acids of the series $C_nH_{2n-2}O_4$, decompose, on distillation with caustic baryta, into hydrocarbons of the formula $C_nH_{2n+2}$ and carbonic acid, viz. :—

$$\text{Suberic acid } C_8H_6O_4 = 2CO_2 + C_6H_{14}.$$
$$\text{Sebacic acid } C_{10}H_{18}O_4 = 2CO_2 + C_8H_{18}.$$

In this way Riche prepared from suberic acid, a hydrocarbon, for which he gives the formula $C_6H_{14}$ and boiling point 76° C, and from sebacic acid, a hydrocarbon $C_8H_{18}$ boiling at 125° C. These hydrocarbons appeared to be isomeric, but not identical with, those obtained from coal tar and American petroleum, their boiling points being much higher, and their odours being, according to Riche, strongly aromatic. Arppe† has, however, lately shown that the acids above-mentioned had not been previously obtained in a pure state; that the substances supposed to be the pure acids were mixtures of different homologous bodies; and that the so-called suberic acid is a mixture of two well crystallisable acids, one having the composition $C_8H_{14}O_4$, for which he retains the name suberic acid, and another having the composition $C_9H_{16}O_4$, to which he gives the name azelaic acid. From this investigation it would appear that the hydrocarbons obtained by Riche cannot be definite compounds, but must consist of mixtures of homologous hydrides: hence, the subject required fresh investigation, and I undertook to repeat Arppe's experiments, commencing with the acids from which the best known of the hydrocarbons, viz., the hydrides of hexyl and heptyl, can be obtained.

The method described by Arppe‡ was strictly adhered to, and the results obtained agreed in all particulars with his.

Castor-oil was heated with nitric acid of sp. gr. of 1·2, as long as any action continued. The solid product was boiled in a large quantity of water, the oil separated, and the mixed acids allowed to crystallise. The crystals were next washed with water, twice recrystallised, and dried at 100°C. The powder thus obtained was repeatedly digested in the cold with ether, azelaic acid being much more soluble in this menstruum than suberic acid. On filtering the solution, and distilling off the ether, the residue was found to give pure crystals of azelaic acid, when rapidly crystallised from water. After repeated treatment with ether, the crude acid ceased to yield crystals of azelaic acid, a white powder being deposited, consisting of a mixture of suberic and azelaic acids. On continuing the treatment with ether for a still longer time, the residue yielded small quantities of needle-shaped crystals of pure suberic acid. The portion of the crude acid left in the flask now consisted of pure suberic acid, which was obtained in crystals when the mass was dissolved in water. According to this method, $2\frac{1}{2}$ kilos. of castor oil yielded about 90 grms. of suberic acid, and 75 grms. of azelaic acid.

---

* Comptes rendus, t. 49, 304; Ann. Ch. Pharm. cxv, 111.

† Ann. Ch. Pharm. cxv, 143.

‡ Ann. Ch. Pharm. cxx, 288; cxxiv, 86.

### *Suberic Acid.*

This acid crystallises in long white needles, melting at 140°C., and solidifying at 138·5° C. The following analytical results were obtained :—

I. 0·5080 grm. substance (dried at 100°C.), burnt with oxide of copper, gave 1·0278 grm. carbonic acid, and 0·3872 grm. water.

II. 0·3420 grm. gave 0·6921 grm. carbonic acid, and 0·2625 grm. water.

| | Calculated. | | Found. | |
|---|---|---|---|---|
| | | | I. | II. |
| $C_8$ | 96 | 55·17 | 55·17 | 55·18 |
| $H_{14}$ | 14 | 8·05 | 8·47 | 8·52 |
| $O_4$ | 64 | 36·88 | — | — |
| | 174 | 100·00 | | |

The silver-salt of this acid retains water for some time at 100°C.; it can, however, all be driven off by continued drying at this temperature.

I. 0·2703 grm. of silver-salt yielded 0·1500 grm. silver.
II. 0·3648 „ „ „ 0·2015 „ „
III. 0·6964 „ „ „ 0·3847 „ „

| Calculated. | Found. | | |
|---|---|---|---|
| | I. | II. | III. |
| $C_8H_{12}O_4$,2Aq. = 55·67 per cent. Aq. | 55·49 | 55·23 | 55·24 |

## *Action of Caustic Baryta on Suberic Acid.*

According to Riche, when suberic acid is heated with excess of caustic baryta, the above mentioned reaction occurs at 80°C. I did not find this statement to be correct, as suberic acid heated either with anhydrous and hydrated baryta, remained unaltered until the temperature rose nearly to a dull red heat. The mass then swells up, and aromatic vapours are given off, which condense into an oily liquid. The best yield was obtained by mixing crystallised suberic acid with dry caustic baryta in excess, adding enough water to form a paste solidifying on cooling, and heating the powdered mixture very slowly in an iron retort, over a gas flame. Water first comes over, and when the temperature has risen nearly to a red heat, thick white vapours appear, which condense into an oily aromatic liquid, floating on the surface of the water. This liquid consists of a mixture of several bodies; the greater portion, however, is unacted upon by a mixture of nitric and sulphuric acids. On the addition of this acid mixture, copious red fumes are evolved, and the liquid becomes strongly heated. The oil remained in contact with the acids several days; it was then distilled off, washed with water, and dried over caustic potash. Rectified over sodium, the greater part of the liquid distilled between 69·5° and 70°C, the thermometer rising at last to 75°. The portion boiling between 69·5° and 70°, when rectified again over sodium, boiled constantly at 69·5° under a pressure of 757·7 mm. The specific gravity of this liquid was found to be 0·6617 at 17·5° compared with water at the same temperature. It is a colourless liquid with a faint smell, closely resembling that of the hydride of hexyl from cannel-oil and petroleum. Its composition is shown to be $C_6H_{14}$ by the following analyses:—

I. 0·2056 grm., burnt with oxide of copper, gave 0·6282 grm. carbonic acid, and 0·2992 grm. water.

II. 0·1497 grm. gave 0·4590 grm. carbonic acid, and 0·2241 grm. water.

| | Calculated. | | Found. | |
|---|---|---|---|---|
| | | | I. | II. |
| $C_6$ | 72 | 83·72 | 83·33 | 83·63 |
| $H_{14}$ | 14 | 16·28 | 16·17 | 16·63 |
| | 86 | 100·00 | 99·50 | 100·26 |

*Azelaic Acid*

crystallises in large thin pearl-white scales, melts at 106°C. and solidifies at 104° to a crystalline mass.

I. 0·5172 grm. substance (dried at 100°C.) gave 1·0949 grm. carbonic acid, and 0·4012 grm. water.

| | Calculated. | | Found. |
|---|---|---|---|
| $C_9$ | 108 | 57·41 | 57·70 |
| $H_{16}$ | 16 | 8·51 | 8·61 |
| $O_4$ | 64 | 34·05 | |
| | 188 | 100·00 | |

The silver-salt of this acid also retains water for a long time, but it may all be got rid of at 100°C. by continued drying.

I. 0·7758 grm. silver-salt gave 0·4146 grm. silver.
II. 0·5366 grm. ,, ,, 0·2865 grm. ,,

| Calculated for the Formula. | | Found. I. | II. |
|---|---|---|---|
| $C_9H_{14}O_4 2Ag$ | 53·73 p. c. Ag | 53·44 | 53·45 |

*Action of Caustic Baryta on Azelaic Acid.*

The process used for azelaic acid was the same as in the case of suberic acid. The decomposition again took place just below a dull red heat. The oily liquid which distilled over was treated with a mixture of concentrated sulphuric and nitric acids as before. A strong action ensued, with the formation of small quantities of nitro-compounds, which were subsequently proved to contain neither nitro-toluol nor nitro-benzol. The quantity of these was, however, not sufficient to admit of further investigation.

The unattacked liquid was separated from the mixed acids, washed with water, dried over potash, and distilled over sodium. It began to boil at 95°C.; the temperature quickly rose to 97°, and nearly the whole came over between that temperature and 100°. The portion boiling between 97° and 100° came over on redistillation almost entirely between 98°—99°. The specific gravity of this liquid was found to be 0·6851 at 17·5°, and the following analyses show it to have the formula $C_7H_{16}$.

I. 0·1640 grm. gave 0·5027 grm. carbonic acid and 0·2360 grm. water.

II. 0·1662 grm. gave 0·5120 grm. carbonic acid and 0·2420 grm. water.

| | Calculated. | Found. I. | Found. II. |
|---|---|---|---|
| $\text{Ȼ}_7$ | 84 | 83·60 | 84·02 |
| $H_{16}$ | 16 | 15·99 | 16·18 |
| | 100 | 99·59 | 100·20 |

From the above experiments it appears that the hydride obtained by Riche from his suberic acid, consisted of a mixture of hydride of hexyl with such a quantity of hydride of heptyl, as considerably to raise the boiling point, without materially altering the per-centage composition, whilst the formation of nitro-compounds proves that the decomposition is not so simple as is expressed by his equation.

The boiling points of the hydrides obtained from the pure acids agree exactly with those found by Schorlemmer in the hydrides of cannel-coal. The specific gravities of the former hydrides are, however, much lower than those of the latter, whilst the specific gravity of the hydride of hexyl from suberic acid agrees closely with that of the β hydride of hexyl of Wanklyn and Erlenmeyer. The yield of hydride does not amount to more than 3 per cent. of the weight of the acid employed, and I am at present engaged in the preparation of large quantities of the pure acids, with the intention of examining the derivatives of these hydrides.

In conclusion, I beg to thank Prof. Roscoe and Mr. Schorlemmer for the valuable aid they have given me in carrying out the above experiments.

## XXX.—*On the Identity of Methyl and Hydride of Ethyl.*

By C. SCHORLEMMER, F.C.S., Assistant in the Laboratory of Owens College, Manchester.

THE hydride of ethyl which served for the following experiments was prepared by the action of concentrated sulphuric acid upon mercuric ethide, which can now be obtained, with the greatest ease, in any wished for quantity, according to the beautiful method discovered by Frankland and Duppa.*

In order to remove the traces of mercuric ethide still contained in the gas, it was washed with Nordhausen sulphuric acid and water. Hydride of ethyl thus prepared is perfectly pure, as the following eudiometric analysis proves:—

| | Vol. | Pressure in M. | Temp. C. | Vol. at 0°C, and 1 M. pressure. |
|---|---|---|---|---|
| Original gas (moist) .................... | 95·0 | 0·2040 | 13·0 | 17·48 |
| After addition of oxygen (moist) .......... | 410·2 | 0 5041 | 13·5 | 195·68 |
| After explosion ........................ | 352·6 | 0·4582 | 11·0 | 151·98 |
| After absorption of carbonic acid (dry)...... | 298 5 | 0·3080 | 11·5 | 117·06 |

| | Found. | Calculated. |
|---|---|---|
| Gas employed ........ | 17·18 | 17·47 |
| Contraction ......... | 43·70 | 43·67 |
| Carbonic acid ........ | 34·92 | 34·94 |

In order to act upon hydride of ethyl with chlorine, I proceeded exactly in the same manner as I have fully described in a paper on the action of chlorine upon methyl, read before the Royal Society.† The phenomena were the same in both cases. The colour of the chlorine disappeared rapidly, whilst oily drops condensed on the sides of the bottles, volatilizing again on gently heating. The products thus formed, after they had been freed from hydrochloric acid, were passed into a receiver surrounded by a freezing mixture. The colourless liquid, which there condensed, consisted chiefly of chloride of ethyl, boiling at 11°C.

0·2080 grm. gave 0·4150 grm. of chloride of silver, and 0·0145 grm. of metallic silver.

| Calculated for $C_2H_5Cl$. | Found. |
|---|---|
| 55·04% of Cl. | 55·2% |

Besides this compound, a smaller quantity of compounds of a higher boiling point was found, from which monochlorinated chloride of ethyl $C_2H_4Cl_2$ boiling at 64°C. could be isolated.

---

* Chem. Soc. Journ. [2], i, 415.

† Proceedings Roy. Soc., xiii, 225.

The results of these experiments differ widely from those of older researches of Frankland and Kolbe, who studied the action of chlorine on the gas obtained by treating cyanide of ethyl with potassium, which they first considered as methyl, but afterwards recognised as hydride of ethyl. Frankland and Kolbe found that when a mixture of one volume of hydride of ethyl and one volume of chlorine was exposed to diffused daylight, one volume of hydrochloric acid, and one volume of a gas of the composition $C_2H_5Cl$, were obtained. This substance was, however, believed not to be identical with chloride of ethyl, because it could not be condensed at $-$ 18°C.*

Frankland showed afterwards that, by the action of two volumes of chlorine upon one volume of hydride of ethyl, a liquid substitution-product was formed, whilst by the action of one as well as two volumes of chlorine upon one volume of methyl, only gaseous chlorine compounds were formed,† a result totally different from that which I obtained.

As my experiments were performed with the moist gases, whilst Frankland and Kolbe employed them in the perfectly dry state, I found it necessary to repeat these latter experiments, exactly under the circumstances described by Frankland and Kolbe, only on a larger scale. I employed strong white glass bottles of exactly the same capacity (about 800 cbc.). One was filled over dry mercury with perfectly dry methyl, another with hydride of ethyl. Each of the bottles, when filled, was connected, by means of perforated well-dried corks, and short, wide glass tubes, with a bottle of the same capacity previously filled with dry chlorine. The bottles thus prepared were left in the dark for sixty hours, in order that the gases might be completely mixed, and after that time they were exposed to diffused daylight. The colour of the chlorine gas soon disappeared, and oily drops condensed on the sides of the bottles, which volatilized on gently heating.

The bottles were opened under dry mercury. No contraction took place, but on adding a little caustic potash and a few drops of water, half the gas, consisting of hydrochloric acid, was absorbed. The remaining gas was displaced by warm mercury, and passed into a reservoir surrounded by a freezing mixture, where a liquid condensed, possessing, in both cases, properties identical with the liquid previously prepared from the moist gases, and consisting mainly of chloride of ethyl. The quantity of this compound obtained from methyl, or hydride of ethyl, was about double that which I got in my former experiments, which larger amount is easily explained by the absence of aqueous liquids, by which a great part of the product is dissolved.

---

* Chem. Soc. Qu J, i, 60.

† Chem. Soc. Qu. J, iii, 337.

It appears from these experiments that what I have formerly proved for the higher terms of the hydrocarbons of the series $C_nH_{2n+2}$, viz., that no chemical difference exists between hydrides and radicles, holds also good for the lowest isomers of these groups. With regard to differences in their physical properties, we find that, like all the isomeric members of these series, they exhibit a close agreement; only methyl appears to be a little less soluble in water than hydride of ethyl. The coefficients of absorption of methyl have been determined by Bunsen,* and of hydride of ethyl by Schickendanz,† who found that the values for hydride of ethyl agree very closely with those which Bunsen found for methyl, and that the curves representing the coefficients of the two gases are nearly parallel, and very near to each other. Schickendanz concludes that, as methyl and hydride of ethyl are isomers, it would appear probable that this relation between the coefficients of absorption of the two gases was not accidental, but caused by their chemical constitution. I believe that the slight difference in the solubility of the two gases, as well as the parallelism of the two curves, will be explained by impurities of the methyl employed by Bunsen, which was prepared by the action of zinc upon iodide of methyl, a method which yields the least pure product;‡ and a small admixture of a foreign gas must exercise a considerable influence on the value of the coefficient of absorption. The gases are also in the same proportions absorbed by alcohol, 1 volume of alcohol dissolving about 1 volume of methyl§ and 1·13 volume of hydride of ethyl.||

Hence it appears that until differences are found between methyl and hydride of ethyl, better marked than those above mentioned, we must consider the hydrocarbons $C_2H_6$ derived from different sources as identical, and as being the hydride of ethyl or deutyl.

---

* Phil Mag., [4], ix, 128.

† Ann. Ch. Pharm, cix, 106.

‡ Chem. Soc. Qu. J., iii, 337.

§ Ibid, ii, 128.

|| Ibid, i, 60.

# XXXI.—*On the Peroxides of the Radicals of the Organic Acids.*

By Sir C. Brodie, Bart., F.R.S., Professor of Chemistry in the University of Oxford.

(Abstracted by the Author from the Philosophical Transactions 1864, p. 407.)

In a former communication* I announced to the Royal Society the discovery of a new group of chemical substances, the peroxides of the radicals of the organic acids—bodies which, in the systems of the combinations of these radicals, occupy the same relative position as is held by the peroxides of hydrogen, barium, or manganese in the systems of the combinations of those elements.

The investigation of these peroxides is attended with peculiar difficulties. It is by no means easy to prepare in any considerable quantity the anhydrous acids and chlorides themselves, which is only the first step in the preparation of the peroxides. The greater number of these substances are also excessively unstable; they are decomposed in the very reactions by which they are produced, and the quantity actually obtained is very far from corresponding to that which is indicated by theory. There can be little hope of a complete and successful investigation of the decompositions of these bodies, until methods are discovered by which the substances themselves can be more readily procured. I have for these reasons not yet been able to submit their transformations to the profound study which the subject merits, and which will doubtless be some day followed by a rich harvest of discovery.

One exception should be made to the above remarks, the peroxide of benzoyl. This beautiful substance can be procured with comparative facility, and I hope to pursue the investigation of its metamorphoses. It appeared to me, however, of primary importance to establish the perfect generality of the fundamental reaction by which these bodies are prepared. This I have effected by forming several members of the group: and I have also, in one instance, at least, succeeded in ascertaining the constitution of the peroxide of a bibasic acid, a member of a new class of chemical substances, fundamentally different (as the chemist would perhaps anticipate) from the peroxides of the monobasic acids, and characterised by well-marked reactions.

---

* Proceedings of the Royal Society, vol. ix, p. 361.

The peroxide of barium, in respect to the definite and universal character of its reactions, may be placed by the side of the alkalies themselves. Every anhydrous organic acid with which I have made the experiment, without any exception, has been found to be converted by its agency into an organic peroxide. It is a new instrument of chemical research, admirable for the power and the simplicity of its action, and which will certainly find, in the future of chemistry, many applications besides those which are here recorded. Its preparation is a matter of importance.

### *Preparation of Peroxide of Barium.*

The peroxide of barium, as prepared by leading oxygen over heated baryta, is useless for the purposes of the following experiments, for the reason that the oxidation of the baryta is never complete, and that the peroxide is mixed with large quantities of the oxide of barium. However, the first step towards the preparation of a pure peroxide is the preparation of a crude material.

When oxygen gas is passed over fragments of baryta heated in a porcelain tube, the absorption of the gas proceeds at first with great rapidity; and if the heat be properly regulated, not a trace of oxygen will pass through the apparatus. It is, nevertheless, extremely difficult to prepare in this manner a peroxide which shall contain more than about 6 parts of oxygen to 100 of baryta, however long the action of the oxygen be continued, the theoretical amount of oxygen required for the formation of the peroxide being 10·46 parts of oxygen to 100 of baryta. By far the simplest and most practical process for the oxidation of baryta is that devised by Liebig, which consists in exposing to a gentle heat an intimate mixture of powdered baryta and chlorate of potassium. The mixture is thrown by degrees into a crucible heated to low redness; an ignition is perceived when the chlorate of potassium melts. The fused mass is powdered and exhausted with water, which leaves an insoluble residue, containing large quantities of peroxide of barium.

On determining the amount of oxygen combined with the baryta in this experiment, I found that the peroxide did not contain above half the theoretical amount of oxygen. Experiments, of which the details are here omitted,* leave no doubt that, in this reaction, the baryta is oxidised to the condition, not of peroxide, but of sesquioxide of barium.

---

* For these see the original memoir.

When lime or strontia was substituted for baryta in the preceding experiment, not a trace of peroxide of hydrogen could be detected in the resulting solution.

To prepare pure peroxide of barium, the crude peroxide, as prepared by either of the above processes, is finely pulverized and rubbed with water in a mortar, so as entirely to convert it into hydrate. It is then mixed gradually with a very dilute solution of hydrochloric acid, care being taken to keep the solution constantly acid. This solution is filtered, and rendered alkaline with a slight excess of baryta-water. The addition of the latter effects the precipitation of the alumina and iron. The alkaline solution, which immediately begins to decompose, is rapidly filtered through linen filters, and to the clear filtrate is added an excess of baryta-water. The hydrated peroxide of barium is precipitated in brilliant plates, which are insoluble in water, and may be washed by decantation. In order to ascertain whether the whole of the peroxide is precipitated, a small portion of the solution may be filtered, rendered acid, and tested with a dilute solution of bichromate of potassium.

The washed precipitate is to be collected on a filter, pressed out between blotting-paper, and dried under the air-pump, by which means the whole of the water of crystallization may be driven off. The dry peroxide appears in the form of a fine white powder, resembling magnesia. I have analysed this substance, and found it to consist of anhydrous peroxide of barium, $Ba_2O_2$, the only impurity being a trace of carbonate. It is in this condition a perfectly stable substance.

The absolute amount of peroxide of barium contained in the different preparations employed in the following experiments, was ascertained either by a direct determination of the oxygen evolved by the action of platinum-black and a dilute acid, or by means of a standard solution of permanganate of potassium, according to the method which I have given in a former paper.

## *Peroxide of Benzoyl*, $C_{14}H_{10}O_4$.

The peroxide of benzoyl is prepared by the action either of the chloride of benzoyl, or of the benzoic anhydride on hydrated peroxide of barium. When the following precautions are taken, the reaction is perfectly definite.

Equivalent quantities are to be weighed out of chloride of benzoyl and pure peroxide of barium. The peroxide of barium is converted into hydrate, and pressed between blotting-paper, to remove any great excess of water; it is then added by degrees to the chloride of benzoyl in a small mortar, and the two substances well mixed by means of a pestle. The mixture is allowed to remain for some hours; and the resulting substance having been mixed with water is thrown on a filter, and washed until the chloride of barium is removed. It is then treated with a weak solution of carbonate of sodium, so as to render the solution decidedly alkaline. After thus removing the benzoic acid, of which a certain portion is always formed in the reaction, the substance is pressed out between blotting-paper, and dried under the air-pump. When perfectly dry, it is to be dissolved in bisulphide of carbon at a temperature not exceeding 35° C, and three or four times crystallized from that fluid. Of several slightly different methods of preparation, this gave by far the most satisfactory results.

If, in the preparation of this substance, the peroxide of barium be taken in excess, that is, more than one equivalent of that peroxide $Ba_2O_2$, to two of chloride of benzoyl, 2BzCl, the amount of peroxide of benzoyl formed is reduced; and if a great excess of peroxide of barium be employed, as for example one equivalent of that substance, $Ba_2O_2$, to one equivalent of chloride of benzoyl, BzCl, oxygen gas is evolved, and hardly a trace of peroxide will be formed. This arises from the circumstance that the reaction by which the peroxide of benzoyl is formed is immediately succeeded by a second reaction in which that substance is destroyed, according to the equations—

$$2BzCl + Ba_2O_2 = 2BaCl + Bz_2O_2,$$
$$Bz_2O_2 + Ba_2O_2 = 2BaBzO + O_2.$$

I have ascertained by direct experiment that the peroxide of barium, when mixed in water with the peroxide of benzoyl, is decomposed, with evolution of oxygen gas.

This affords a striking example of a class of decompositions which I recently brought before the Society,—in which one equivalent of the peroxide of barium acts as an agent of oxidation, while a second equivalent acts as a reducing agent, destroying the substance formed in the first reaction.

The peroxide of benzoyl thus prepared is in splendid crystals.

From large quantities of solution I have occasionally obtained these crystals as much as three-fourths of an inch in diameter. They are referable to the right prismatic system, and their form, as crystallised from ether, has been examined by Professor W. H. Miller, of Cambridge.* It is difficult to ascertain with absolute accuracy the melting-point of this substance. The point of decomposition lies close upon the melting-point; and it is only in very small quantities that it can be melted without being decomposed. My experiments, however, place the melting-point at 103·5° C. At 15°. C. 100 parts of bisulphide of carbon dissolve 2·53 parts of the peroxide of benzoyl. It is also soluble in ether and benzol.

This substance gave on analysis the following results :—

| | I. | II. | The numbers required by theory are | | |
|---|---|---|---|---|---|
| Carbon...... | 69·31 | 69·31 | $C_{14}$ = | 168 | 69·42 |
| Hydrogen..... | 4·23 | 4·18 | $H_{10}$ = | 10 | 4·13 |
| Oxygen...... | 26·46 | 26·51 | $O_4$ = | 64 | 26·45 |
| | 100·00 | 100·00 | | 242 | 100·00 |

When the peroxide of benzoyl is boiled with a solution of hydrate of potassium, oxygen gas is evolved and benzoate of potassium is formed—

$$2Bz_2O_2 + 4KHO = 4BzKO + 2H_2O + O_2.$$

If the peroxide of benzoyl be heated, it is decomposed with a slight explosion. By mixing the finely powdered peroxide with sand, the action may be moderated; under these circumstances carbonic acid is evolved. The decomposition commences at about 85° C. I have estimated the loss of weight which the substance undergoes in this decomposition: in two experiments 100 parts of peroxide lost 18·6 and 18·18 parts; in three other experiments somewhat lower numbers were obtained, 17·78, 16·56, and 16·7 per cent. The theoretical loss, if one equivalent of carbonic anhydride, $CO_2$, were evolved from one equivalent of the peroxide, $C_{14}H_{10}O_4$, would be 18·18 per cent. The substance formed by the removal of one equivalent of carbonic anhydride from the peroxide of benzoyl, $C_{13}H_{10}O_2$, would be isomeric with the benzoate of phenyl.

---

* See Proceedings of the Royal Society, January 15, 1862.

I have not, however, yet succeeded in so moderating the action as to form only one substance. During the decomposition a small quantity of benzoic acid sublimes, and on exhausting the sand with ether, filtering, and evaporating the ethereal solution, a soft glutinous residue is obtained, of which a portion dissolves on prolonged boiling in water. Benzoic acid passes over with the vapour of the water, and ultimately a hard and perfectly transparent resin remains, which is soluble in potash, and in all respects resembles a natural resin. I hope again to recur to this substance.

If peroxide of benzoyl be treated with a large excess of concentrated nitric acid, it is dissolved by the acid. When this solution is poured into water, a slightly yellow flocculent substance separates, which, dried under the air-pump, is soluble in bisulphide of carbon.

3 grms. of peroxide of benzoyl were thrown into about 3 fluid-ounces of fuming nitric acid, specific gravity 1·505. There was no perceptible increase of temperature or evolution of gas. The peroxide was rapidly dissolved, the mixture became deeper in colour, and after some time the vessel was filled with fumes of hyponitric acid. After standing about twenty-four hours, the solution in nitric acid was mixed with ten times its bulk of water. The precipitate formed was collected on a filter and washed free from acid. It was then dried under the air-pump, and dissolved in bisulphide of carbon. On the cooling of the bisulphide, a slightly yellow flocculent body separated. This was again dried under the air-pump and analysed.

The formula of the substance derived from the peroxide of benzoyl by the substitution of two atoms of peroxide of nitrogen, $NO_2$, for two atoms of hydrogen, H, is $C_{14}H_8(NO_2)_2O_4 = C_{14}H_8N_2O_8$, and requires—

| | Found. | | | Required. |
|---|---|---|---|---|
| Carbon.......... | 50·60 | $C_{14}$ | = 168 | 50·60 |
| Hydrogen ....... | 2·58 | $H_8$ | = 8 | 2·41 |
| Nitrogen ........ | 8·49 | $N_2$ | = 28 | 8·43 |
| Oxygen.......... | 35·33 | $O_8$ | = 128 | 38·56 |
| | 100·00 | | 332 | 100·00 |

This body, when heated, decomposes with a slight explosion, leaving a resinous matter similar in appearance to that formed by the decomposition of the peroxide of benzoyl.

## *Peroxide of Cumenyl.*

The peroxide of barium is decomposed by the chloride of cumenyl precisely as by the chloride of benzoyl. The resulting substance crystallizes from ether in long and beautiful needles; when heated it explodes, leaving a resinous residue.

I have only once prepared this substance, and did not succeed in procuring it in a state of absolute purity.

Analysis gave—

| | |
|---|---|
| Carbon .......... | 73·24 |
| Hydrogen ........ | 7·00 |
| Oxygen ..... .... | 19·76 |
| | 100·00 |

The formula $C_{20}H_{22}O_4$ requires—

| | | |
|---|---|---|
| $C_{20}$ = | 240 | 74·23 |
| $H_{22}$ = | 22 | 6·75 |
| $O_4$ = | 64 | 19·02 |
| | 326 | 100·00 |

## *Peroxide of Acetyl.*

In the preparation of the peroxides of the acetic series, the use of the anhydrous acid has great advantages over the use of the corresponding chloride. By the action of the anhydride of the acid on peroxide of barium, I have succeeded in preparing three of these peroxides, the peroxides of acetyl, butyl, and valeryl.

The peroxide of acetyl is prepared by dissolving anhydrous acetic acid in pure ether, and adding gradually to this solution an equivalent quantity of peroxide of barium.

The decomposition takes place according to the equation—

$$2C_4H_6O_3 + Ba_2O_2 = 2C_2H_3BaO_2 + C_4H_6O_4.$$

The reaction is attended with an elevation of temperature which causes the ether to boil; the temperature is not to be allowed to reach this point. After standing for some time, the solution is filtered from the gelatinous residue, which does not contain a trace of peroxide of barium, and the ether is distilled off at a very low temperature, great care being taken not to allow the temperature to rise towards the end of the operation. The residue, washed first with water and then with a very weak solution of carbonate of sodium, appears as a thick and viscid fluid, which solidifies to a mass of minute crystals, when the tube containing it is placed in ice. I have in this manner experimented on as much as 20 grms. of anhydrous acetic acid, dissolved in about four times its bulk of pure ether. The addition of the equivalent quantity of peroxide of barium occupied two hours. From these 20 grms. of anhydrous acetic acid, only as much peroxide of acetyl was procured as to be sufficient for the two following determinations. The analysis was thus affected :—

An undetermined quantity of the peroxide of acetyl was placed in a little water at the bottom of a small flask, with a bulb attached to it, somewhat similar to those occasionally used for the estimation of carbonic acid. The bulb was filled with baryta-water, a small tube containing platinum-black introduced into the apparatus, and the whole was weighed. The peroxide was now decomposed by allowing the baryta-water to flow into the flask from the bulb. Acetate of barium and peroxide of barium are formed. The peroxide of barium was decomposed by bringing the platinum-black contained in the small tube in contact with it. After the completion of the reaction, the apparatus was again weighed, and thus the loss of oxygen was determined.

A current of carbonic acid was now passed through the solution, which was boiled and filtered, and the barium estimated as sulphate. The sulphate of barium thus formed is the measure of the acetate produced by the decomposition of the peroxide of acetyl.

Experiment I. The weight of the apparatus before and after the experiment gave a loss of oxygen of 0·1225 grm.

The solution precipitated by sulphuric acid gave 1·776 grm. of sulphate of barium.

Experiment II. The loss of oxygen estimated as before was 0·137 grm.

The solution precipitated by sulphuric acid gave 1·914 grm. of sulphate.

In Experiment I, 100 parts of sulphate being formed, 6·89 parts of oxygen were evolved.

In Experiment II, 100 parts of sulphate were obtained and 7·01 of oxygen evolved.

Theory requires that for every 100 parts of sulphate of barium formed, 6·86 parts of oxygen should be evolved.

When a small drop of the peroxide of acetyl is heated in a watch-glass, it is decomposed with an explosive violence, only to be paralled by the decomposition of chloride of nitrogen. Hence the greatest care is necessary in its preparation, especially during the distillation of the ether in which it is dissolved. I had frequently effected this operation without accident; but on one occasion my assistant was engaged in distilling off the ether from a rather considerable quantity of the substance, which was contained in a flask placed in warm water on a small copper water-bath; the temperature was probably allowed to rise too high, and towards the close of the operation a violent explosion took place with a report as of a cannon. A large hole was made in the copper water-bath, through which the hand might be passed, the copper being folded back upon the sides of the bath. The explosion, though of excessive violence, was local, and nothing in the laboratory in which the explosion took place was injured.*

The peroxide of acetyl is readily decomposed under the influence of sunlight. A measured quantity of the substance was kept unaltered in bulk for above eighteen hours in the dark, but when placed in water in the bright sunlight, the same substance rapidly disappeared.

This peroxide is a most powerful agent of oxidation; like chlorine it rapidly bleaches indigo; it separates iodine from hydriodic acid and from iodide of potassium; it converts a solution of ferrocyanide of potassium into ferricyanide; and immediately oxidises the hydrated protoxide of manganese.

These properties it has in common with the peroxide of hydrogen; but it is readily distinguished from that substance by not producing the peculiar effects of reduction by which the peroxide of hydrogen is characterised. It does not reduce an acid solution of chromic or permanganic acids. The addition of baryta-water to the peroxide of acetyl suspended in water, causes an immediate precipitate of crystals of the hydrated peroxide of barium.

---

* Since the first publication of this paper, I have had an accident in the preparation of the peroxide of acetyl, which shows the excessive care required in dealing with it. I had in my hand a small thin glass tube, containing perhaps 40 drops of the peroxide, which had just been removed from the solution in which it had been procured. I was engaged in projecting into it some very small pieces of chloride of calcium. Five or six pieces had been thrown in, when, on the addition of the next piece, the substance exploded with terrific violence, driving the glass in minute fragments into my hands. The concussion of the air produced bruises on the eyes and face, and several small fragments of the glass tube were deeply embedded in the hands and face. If I had been operating with two or three times the quantity of the peroxide, the accident would, undoubtedly, have been of a most serious nature. I may observe that I had never before seen the substance explode without the application of considerable heat, and that I had repeatedly dried the peroxide of butyl in a similar manner with chloride of calcium, without effecting its decomposition.

We can have no more convincing proof, if such proof were needed, than that furnished by this experiment, that the difference of properties which oxygen manifests in its different combinations is due, not, as has been imagined, to the existence of certain distinct varieties of that element, but to the circumstance that the combining properties of oxygen, as of other elements, vary with the nature of the chemical substances with which it is combined or associated

### *Peroxide of Butyl.*

The butylic peroxide is readily prepared by mixing hydrated peroxide of barium with anhydrous butyric acid. Experiments made with the view of preparing this substance by the action, in ether, of the dry peroxide of barium on anhydrous acid, were unsuccessful.

The result of this reaction is given in the equation

$$2C_8H_{14}O_3 + Ba_2O_2 = 2C_4H_7BaO_2 + C_8H_{14}O_4.$$

The experiment may be advantageously conducted as follows :—

The anhydrous acid is placed in a small mortar, and an equivalent quantity of hydrated peroxide of barium, from which any great excess of water has been removed, is gradually added to it, the whole being well mixed after each addition of the peroxide. An excess of peroxide of barium is to be carefully avoided, as it again decomposes the peroxide of butyl. To this end it is desirable towards the close of the operation, to examine from time to time the contents of the mortar, by placing a drop on a watch-glass, acidifying with hydrochloric acid, and testing with a dilute solution of bichromate of potassium. The appearance of a feeble blue colour indicates that sufficient peroxide has been added. The substance is mixed with a small quantity of water, and the solution agitated repeatedly with ether, which dissolves the peroxide of butyl. This operation is readily effected in a burette provided with a glass stopcock. The ethereal solution is then repeatedly washed, first with dilute hydrochloric acid, then with a weak solution of carbonate of sodium, until it has a strong alkaline reaction, and then again with water until the alkaline reaction disappears. The solution is filtered and allowed to evaporate in a current of air at a low temperature. An oily residue is left, which is to be washed once or twice with a small quantity of water, in which it is only slightly soluble. It is then removed with a pipette, and allowed to stand for some time in contact with a few fragments of chloride of calcium. The substance thus prepared is pure peroxide of butyl.

This peroxide was analysed with oxide of copper in the usual manner.

Two analyses gave per cent.,

| | I. | II. | Theory requires | |
|---|---|---|---|---|
| Carbon...... | 55·21 | 55·11 | $C_8 = 96$ | 55·172 |
| Hydrogen.... | 8·29 | 8·28 | $H_{14} = 14$ | 8·016 |
| Oxygen...... | 36·50 | 36·61 | $O_4 = 64$ | 36·782 |
| | 100·00 | 100·00 | 174 | 100·000 |

A drop of the peroxide of butyl heated on a watch-glass decomposes with a slight explosion. Suspended in water, it possesses the oxidizing properties of the acetic peroxide.

## *Peroxide of Valeryl.*

The peroxide of valeryl is prepared by the action of anhydrous valerianic acid on hydrated peroxide of barium, the result of the reaction being expressed by the equation

$$2C_{10}H_{18}O_3 + Ba_2O_2 = 2C_5H_9BaO_2 + C_{10}H_{18}O_4.$$

The method of preparation is in all respects the same as that by which the peroxide of butyl is prepared.

The peroxide of valeryl is a dense oily fluid, heavier than water. It gives a slight explosion when heated, and possesses the oxidising properties of the other analogous peroxides.

The substance dried by means of chloride of calcium was analysed with the following results:—

| | I. | II. | Theory requires | |
|---|---|---|---|---|
| Carbon........ | 59·05 | 59·39 | $C_{10} = 120$ | 59·10 |
| Hydrogen .... | 9·17 | 9·17 | $H_{18} = 18$ | 8·91 |
| Oxygen ...... | 31·78 | 31·44 | $O_4 = 64$ | 31·69 |
| | 100·00 | 100·00 | 202 | 100·00 |

### *Peroxide of Camphoryl.*

The action of the anhydrides of the bibasic acids on the alkaline peroxides affords a remarkable illustration of the profound difference by which this group is distinguished from the anhydrides of the monobasic acids. In the latter case we have seen that the monobasic anhydride decomposes with the alkaline peroxide, forming the peroxide of the radical and the barium-salt of the corresponding acid. In the case of the bibasic anhydride, a combination takes place of the anhydride with the peroxide, with the formation of a new and peculiar compound, which we may regard as the barium-salt of the peroxide of the bibasic radical. The compounds thus formed have but little permanence; and although in several cases we have evidence of their formation, in only one example, namely that of camphoric acid, have I been able to effect the analysis of the compound.

If hydrated peroxide of barium be gradually added to anhydrous succinic acid, and carefully mixed with it in a small quantity of water, the mixture becomes fluid; but long before the addition of the equivalent quantity of peroxide of barium, oxygen gas is evolved. If the fluid be filtered when this effervescence commences, it will be found to have the following properties:—

1. The solution is alkaline. It may be assumed, therefore, to contain but little, if any, succinate of barium, which is insoluble in water.

2. The solution, rendered acid, gives no blue colour with bichromate of potassium, and does not discolour permanganic acid. It therefore contains no peroxide of hydrogen. If peroxide of barium be mixed with hydrated succinic acid, a solution is obtained, containing peroxide of hydrogen with the above characteristic reactions.

3. The solution bleaches indigo, gives a precipitate of peroxide of manganese with a solution of acetate of manganese, oxidises ferrocyanide of potassium, and evolves chlorine when boiled with hydrochloric acid.

4. When the solution is boiled, oxygen gas is evolved, and a crystalline precipitate formed of succinate of barium.

Similar results are obtained if hydrated peroxide of barium be mixed with lactide, the lactic anhydride. The peroxide is rapidly dissolved, and a powerfully bleaching solution is obtained, possessing the same oxidising properties as that procured from succinic anhydride. The solution is, however, excessively unstable; even when cooled by ice, it is in a constant state of decomposition, and although it doubtless contains the lactic peroxide, I have been unable to effect its analysis.

With the camphoric anhydride I have been somewhat more successful. The anhydrous camphoric acid used in the following experiments, was prepared by the oxidation of camphor by means of nitric acid. It is better not to attempt the prior preparation of a pure camphoric acid, which is attended with much difficulty, but after the product of the oxidation of camphor has been once or twice crystallised, to distil the crude acid. After two distillations and two or three crystallisations from alcohol of the distilled product, the camphoric anhydride is obtained quite pure.

A portion (about 3 grms.) of anhydrous camphoric acid thus prepared, was triturated in a mortar with ice-cold water, and the equivalent quantity of hydrated peroxide of barium was gradually added to the same, fragments of ice being mixed with the solution. No evolution of gas was observed during the experiment. The filtered solution was rather alkaline, doubtless from the trace of baryta present in the peroxide. The solution, rendered acid, had the following properties. It gave no blue reaction with chromic acid, nor did it discolour permanganic acid. It bleached indigo, oxidised ferrocyanide of potassium, and decomposed hydriodic acid. The residue from which the solution was filtered was small in amount, and contained a little peroxide of barium. The solution when boiled evolves oxygen. Evaporated to dryness, it leaves a residue, which, dissolved in water, gives a precipitate with a solution of acetate of lead. This precipitate was suspended in water, and decomposed by sulphide of hydrogen. The acid thus separated was analysed after one crystallisation. It was pure camphoric acid.

A solution of the camphoric peroxide thus prepared was analysed in the following manner:—

1. A measured quantity of the solution was rendered acid, and titred by means of a standard solution of iodine.

2. To another measured quantity of the same, a solution of carbonic acid in water was added. The liquid was raised to the boiling-point, filtered, and precipitated by sulphuric acid. The addition of the carbonic acid effects the removal of a small quantity of baryta, invariably present through the decomposition of the peroxide of barium.

3. Another portion of the solution, similarly treated, was precipitated by acetate of lead, and the precipitate collected and weighed. The precipitate thus obtained is pure camphorate of lead.

The results thus obtained agree with the hypothesis that the solution contains the substance $C_{10}H_{14}O_5Ba_2$,—the reaction taking place according to the equation,

$$C_{10}H_{14}O_3 + Ba_2O_2 = C_{10}H_{14}O_5Ba_2.$$

For we should have, assuming the camphoric acid to be correctly determined by precipitation with acetate of lead, in 1000 parts of the solution,

Experiment I.

| | Atomic weight. | Ratio calculated. | Found. |
|---|---|---|---|
| $C_{10}H_{14}O_3$ .... | 182 | 25·12 | 25·12 |
| O .... | 16 | 2·20 | 2·07 |
| $Ba_2O$ .... | 153 | 21·12 | 21·51 |

Experiment II.

| | | | |
|---|---|---|---|
| $C_{10}H_{14}O_3$ .... | 182 | 21·13 | 21·43 |
| O .... | 16 | 1·88 | 1·96 |
| $Ba_2O$ .... | 153 | 18·00 | 17·88* |

The oxygen-determinations show that, even in this case, there is a gradual, although but slight, decomposition of the substance taking place during the time which the determinations occupy. But this peroxide is far more stable than the corresponding succinic and lactic peroxides. I have made several unsuccessful attempts to analyse these substances by methods similar to the above; but, from the excessive instability of the solutions, I have been obliged to abandon the attempt. In the case of the lactic peroxide, for example, three successive determinations required 60·8, 54·3, and 48·6 cub. centims. of the standard iodine-solution, showing so rapid a change as to render hopeless the accurate determination of the oxygen. These substances stand, as it were, upon the very verge of chemical possibility, and have only a momentary and fugitive existence.

---

[*] Mean of two determinations 16·5 and 19·22.

That in the above reaction the oxygen is transferred from the peroxide of barium to the anhydrous camphoric acid—in other words, that the compound formed is to be regarded as the barium-salt of the peroxide of camphoryl, and not as the camphorate of the peroxide of barium, is shown by the reactions of the solution. The action of acids upon it does not form peroxide of hydrogen, and the action of alkalies does not reproduce the peroxide of barium. These reactions would take place if the solution contained the salt of the peroxide.

The analogy of the bisulphide of carbon to the anhydrous acids induced me to try its action on the alkaline peroxide. When bisulphide of carbon suspended in water is agitated with hydrated peroxide of barium, the peroxide is dissolved, with formation of a yellow solution. The solution when filtered is at first clear; but on standing, and more rapidly on boiling, a precipitate of carbonate of barium is formed. The solution contains a sulphide of barium. If sulphide of hydrogen be passed through water in which peroxide of barium is suspended, a clear yellow solution is formed similar in appearance to the preceding.

I have not fully investigated the reaction, but the experiments point to the conclusion that, in the first instance, we have formed the combination of bisulphide of carbon and peroxide of barium, which subsequently decomposes into carbonate of barium and bisulphide of barium, according to the equations,

$$CS_2 + Ba_2O_2 = Ba_2CS_2O_2,$$
$$Ba_2CS_2O_2 + 2BaHO = Ba_2CO_3 + Ba_2S_2 + H_2O.$$

The reaction is undoubtedly complicated by the action of the bisulphide of barium on the peroxide. This solution, in presence of an excess of peroxide, becomes colourless, hyposulphite of barium being probably formed—

$$Ba_2S_2 + 3Ba_2O_2 + 3H_2O = Ba_2S_2O_3 + 6BaHO.$$

In the case of the action of carbonic acid on peroxide of barium, I could detect no indication of the formation of a higher oxide of carbon.

The previous investigation has placed beyond doubt the existence of a new and extensive group of chemical substances, the peroxides of the radicals of the organic acids, a group in all probability as numerous as the anhydrides of the acids, and characterised by singular properties, which have never hitherto been discovered in any combination of carbon, and which greatly enlarge our view of the system of analogies by which the organic and inorganic worlds of chemistry are connected.

The transition is obvious from the peroxide of the acid radical to the peroxide of the basic radical. The question is immediately suggested whether, by corresponding processes, we may not be able to procure the peroxides of ethyl, of ethylene, of the compound ammoniums. I am yet occupied with this subject, and will now only remark that the peroxide of the glycol series appears undoubtedly to be formed. The bromide of ethylene does not, indeed, decompose the hydrated peroxide of barium; but this peroxide is immediately acted on by the diacetate, and a solution is formed having a most pungent odour, containing no peroxide of hydrogen, but possessing the usual characteristics of the organic peroxides. I have not made many experiments with the compound ammonias. A solution of hydrated oxide of tetramylammonium, evaporated *in vacuo* with a solution of pure peroxide of hydrogen, gave a residue which did not appear to contain even a trace of a substance resembling an alkaline peroxide. But this by no means renders it impossible that the same experiment may in other cases be more successful; for great differences are found in the stability of the peroxides of very analogous metals; the peroxide of potassium is quite decomposed on evaporation *in vacuo*, whereas the hydrated peroxide of sodium can be readily thus obtained.

## XXXII.—*The Organic Peroxides Theoretically considered.*

By Sir B. C. Brodie, Bart., F.R.S., Professor of Chemistry in the University of Oxford.

[A Discourse delivered before the Fellows of the Chemical Society of London, May 5, 1864.]

Until very recently, the forms of combination of the chemical elements were considered to be limited only by the atomic law. The theory of Dalton was a system of extreme simplicity. In it the elements were regarded as the primary forms of chemical existence, and were supposed to consist of single particles or atoms.

Next in order of simplicity came the secondary compounds, water, hydrochloric acid, and ammonia, in which the elemental atoms were considered to be combined two and two. Then came ternary and quaternary combinations, and so on to more complex forms. On these views each elemental atom had, so to say, the same chemical function, and was capable of forming similar combinations, of the same order and degree of complexity.

Modern chemistry has profoundly modified these early doctrines, which indeed were mere speculation, and had no counterpart in the system of nature. The investigations of the chemists of our day have brought to light facts unknown to Dalton, chemical changes and properties of combination of the elemental bodies, which have given rise to a new order of chemical ideas, and, to say the least, have rendered necessary a complete revision of the atomic theory.

One of the most important results of these inquiries has been the introduction of a new principle of classification; according to which, chemical substances are arranged in natural orders, characterised by similar combining properties. This principle, which, in the system of typical classification, has for some time been applied to compound substances, has recently been extended to the elemental bodies. We have been led to recognize distinctions in the combining properties of the different elements, precisely the same in kind as those which characterise compound substances; which preclude us from regarding them as constituting a single homogeneous system, and compel us, if we would be consistent, to divide them into groups, and to associate them with other substances in our method of classification.

The elements, so far as we may venture, with our present imperfect knowledge, to hazard an opinion, constitute six natural orders, of which hydrogen, mercury, chlorine, oxygen, nitrogen, and carbon, may be taken as typical representatives. Now, the electropositive elements hydrogen and mercury are connected by numerous analogies with certain compound substances, so that, by a natural classification, we group together hydrogen and potassium with the monatomic hydrocarbons, ethyl and marsh gas; and mercury and lead with the diatomic hydrocarbons, ethylene and propylene. But the other elemental groups represented by chlorine, oxygen, nitrogen, and carbon, have not yet been similarly connected with any systems of compound substances.

I am about to trace out the analogies which connect the electronegative elements, chlorine, iodine, and bromine, with the system of organic peroxides, and to show that a similarity of properties exists between these groups of substances, the same in kind as that which is found in the two groups of electropositive elements and the two systems of hydrocarbons, and yet closer in degree.

As I am anxious to render evident that the question at issue is of a real and not a verbal nature, I shall endeavour to treat the subject with as little reference as possible to any special theory or notation, and only to assume facts which are generally admitted.

The classification of chemical substances in natural orders ultimately depends on the classification of chemical reactions, or, since the result of every chemical change may be expressed in the form of an equation, on the classification of chemical equations.

Thus, for example, if we have placed before us the system of equations:—

$$\begin{aligned}
2HCl &= H_2 + Cl_2.\\
2H_2O &= 2H_2 + O_2.\\
2H_3N &= 3H_2 + N_2.\\
2HBr &= H_2 + Br_2.\\
2HI &= H_2 + I_2.\\
2H_2S &= 2H_2 + S_2.\\
2C_2H_4O &= 2C_2H_4 + O_2.\\
2C_2H_4O_2 &= 2C_2H_4O + O_2.\\
2C_2H_5I &= C_4H_{10} + I_2.\\
2H_3P &= 3H_2 + P_2.
\end{aligned}$$

We perceive that these equations may be arranged in groups, thus:—

$$\begin{aligned}
\text{I.}\quad 2HCl &= H_2 + Cl_2.\\
2HI &= H_2 + I_2.\\
2C_2H_5I &= C_4H_{10} + I_2.\\
2HBr &= H_2 + Br_2.
\end{aligned}$$

$$\begin{aligned}
\text{II.}\quad 2H_2O &= 2H_2 + O_2.\\
2C_2H_4O &= 2C_2H_4 + O_2.\\
2C_2H_4O_2 &= 2C_2H_4O + O_2.\\
2H_2S &= 2H_2 + S_2.
\end{aligned}$$

$$\begin{aligned}
\text{III.}\quad 2H_3N &= 3H_2 + N_2.\\
2H_3P &= 3H_2 + P_2.
\end{aligned}$$

And we may proceed to classify the substances which appear in these reactions, as follows:

| | | | | | | |
|---|---|---|---|---|---|---|
| $H_2$ | $O_2$ | $N_2$ | $Cl_2$ | $H_2O$ | $HCl$ | $H_3N$. |
| $C_2H_4$ | $S_2$ | $P_2$ | $I_2$ | $C_2H_4O$ | $HI$ | $H_3P$. |
| $C_2H_4O$ | | | $Br_2$ | $C_2H_4O_2$ | $HBr$ | |
| $C_4H_{10}$ | | | | $H_2S$ | $C_2H_5I$. | |

In these groups, substances which are chemically analogous, are associated together. Thus, iodine and bromine are to be regarded as analogous to chlorine, because they stand in the same relation to hydriodic and hydrobromic acids, as chlorine to hydrochloric acid; and, for similar reasons, ethylene and aldehyde are to be regarded as analogous to hydrogen, for these substances stand to the oxide of ethylene and to acetic acid, in the same chemical relation as hydrogen to water.

Now, comparing ammonia with water, we may ask what substance, if any, stands to ammonia in the same chemical relation as oxygen to water. No such substance has been discovered; but the formula of the substance, if such should exist, is readily ascertained. It is given in the equation

$$2H_3N = 2H_2 + H_2N_2,$$

which is similar in form to the equation

$$2H_2O = 2H_2 + O_2.$$

If, again, we ask, comparing ammonia with hydrochloric acid, what substance in the case of ammonia is analogous to chlorine in the case of hydrochloric acid, the formula of the substance is given by constructing the equation

$$2H_3N = H_2 + H_4N_2$$

similar in form to the equation

$$2HCl = H_2 + Cl_2.$$

Now, the substances $H_2N_2$ and $H_4N_2$ have never been procured; for ammonia, so far as we are aware, is not capable of being thus decomposed. But if decompositions of this nature were discovered, the substance $H_2N_2$ would be classified with oxygen, and $H_4N_2$ with chlorine, on precisely the same principles as sulphur and iodine are classified with those elements; and ammonia would appear in our classification in three places; in one, associated with water; in another, with hydrochloric acid; and, in a third place, in which neither of these substances would appear with it. The three formulæ $H(H_2N)$, $H_2(HN)$, $H_3N$, which at different times have been assigned to ammonia, and express its different chemical aspects, correspond to the three places which ammonia would occupy in this classification.

The substance $H_4N_2$ is in a certain sense represented by the radical cacodyl, which stands to the arsenic base in the same relation as the hypothetical radical amidogen to ammonia, thus—

$$2H_3N = H_2 + H_4N_2$$
$$2H(CH_3)_2As = H_2 + (CH_3)_4As_2,$$

and it would, undoubtedly, be possible to show many points of resemblance between cacodyl and chlorine; such, for example, as the similarity in constitution of the cyanide of cacodyl, the oxide of cacodyl, and cacodylic acid, to the chloride of cyanogen, the oxide of chlorine, and hydrated chlorous acid. It is not to be expected that these analogies should be of a profound character, for the arsenic base has only a very remote resemblance to hydrochloric acid.

If we make a similar comparison between water and hydrochloric acid, and ask what substance has the same relation in regard to water as chlorine in regard to hydrochloric acid, we infer from the equation

$$2H_2O = H_2 + H_2O_2,$$

which is similar in form to the equation

$$2HCl = H_2 + Cl_2,$$

that that substance is the peroxide of hydrogen.

By an obvious extension of these principles, we may inquire what substances are analogous to chlorine in the case of substances analogous to water Now, the analogues of water are substances of such a nature, that if $M$ be the weight of a molecule of the substance, and $M_1$, the molecular weight of the analogue of hydrogen in the substance

$$2M = 2M_1 + O_2,$$

and the analogue of chlorine in the case of that substance, is ascertained from the equation

$$2M = M_1 + M_2,$$

where $M_{11}$ is its molecular weight.

In the annexed Table I have selected a few examples, from the many which might be given in illustration of equations of these forms, the greater number of which represent decompositions which have been actually realised, while others are hypothetical, and given by way of illustration of reactions analogically probable.

| | I. | | II. |
|---|---|---|---|
| $2M$ | $=2M_1 + O_2$ | $2M$ | $=M_1 + M_2$ |
| | | $2HCl$ | $=H_2 + Cl_2$ |
| | | $2HI$ | $=H_2 + I_2$ |
| $2H_2O$ | $=2H_2 + O_2$ | $2H_2O$ | $=H_2 + H_2O_2$ |
| $2K_2O$ | $=2K_2 + O_2$ | $2K_2O$ | $=K_2 + K_2O_2$ |
| $2HKO$ | $=2HK + O_2$ | $2HKO$ | $=HK + HKO_2$ |
| Ether.<br>$2C_4H_{10}O$ | $=2C_4H_{10} + O_2$ | $2C_4H_{10}O$ | $=C_4H_{10} + C_4H_{10}O_2$ |
| Alcohol.<br>$2C_2H_6O$ | $=2C_2H_6 + O_2$ | $2C_2H_6O$ | $=C_2H_6 + C_2H_6O_2$ |
| Baryta.<br>$2BaO$ | $=2Ba^* + O_2$ | $2BaO$ | $=Ba + BaO_2$ |
| Oxide of Ethylene.<br>$2C_2H_4O$ | $=2C_2H_4 + O_2$ | $2C_2H_4O$ | $=C_2H_4 + C_2H_4O_2$ |
| Glycol.<br>$2C_2H_6O_2$ | $=2C_2H_6O + O_2$ | $2C_2H_6O_2$ | $=C_2H_6O + C_2H_6O_3$ |
| $2Cl_2O$ | $=2Cl_2 + O_2$ | $2Cl_2O$ | $=Cl_2 + Cl_2O_2$ |
| $2Cl_2O_2$ | $=2Cl_2 + O_2$ | $2Cl_2O_2$ | $=Cl_2O + Cl_2O_3$ |
| $2Cl_2O_3$ | $=2Cl_2O_2 + O_2$ | $2Cl_2O_3$ | $=Cl_2O_2 + Cl_2O_4$ |
| $2HClO$ | $=2HCl + O_2$ | $2HClO$ | $=HCl + HClO_2$ |
| $2HClO_2$ | $=2HClO + O_2$ | $2HClO_2$ | $=HClO + HClO_3$ |
| $2HClO_3$ | $=2HClO_2 + O_2$ | $2HClO_3$ | $=HClO_2 + HClO_4$ |
| Acetic Anhydride.<br>$2C_4H_6O_3$ | Acetyl.<br>$=2C_4H_6O_2 + O_2$ | $2C_4H_6O_3$ | Acetic Peroxide.<br>$=C_4H_6O_2 + C_4H_6O_4$ |

* Ba = 137·0.

Butyric Anhydride. Butyryl. Butyric Peroxide.

$$2C_8H_{14}O_3 = 2C_8H_{14}O_2 + O_2 \qquad 2C_8H_{14}O_3 = C_8H_{14}O_2 + C_8H_{14}O_4$$

Valerianic Anhydride. Valeryl. Valerianic Peroxide.

$$2C_{10}H_{18}O_3 = 2C_{10}H_{18}O_2 + O_2 \qquad 2C_{10}H_{18}O_3 = C_{10}H_{18}O_2 + C_{10}H_{18}O_4$$

Acetic Acid. Aldehyde. Glycolic Acid.

$$2C_2H_4O_2 = 2C_2H_4O + O_2 \qquad 2C_2H_4O_2 = C_2H_4O + C_2H_4O_3$$

Benzoic Anhydride. Benzoyl. Benzoic Peroxide.

$$2C_{14}H_{10}O_3 = 2C_{14}H_{10}O_2 + O_2 \qquad 2C_{14}H_{10}O_3 = C_{14}H_{10}O_2 + C_{14}H_{10}O_4$$

Cuminic Anhydride. Cumenyl. Cuminic Peroxide.

$$2C_{20}H_{22}O_3 = 2C_{20}H_{22}O_2 + O_2 \qquad 2C_{20}H_{22}O_3 = C_{20}H_{22}O_2 + C_{20}H_{22}O_4$$

$$2CO_2 = 2CO + O_2 \qquad 2CO_2 = CO + CO_3$$

$$2SO_3 = 2SO_2 + O_2 \qquad 2SO_3 = SO_2 + SO_4$$

$$2H_2SO_4 = 2H_2SO_3 + O_2 \qquad 2H_2SO_4 = H_2SO_3 + H_2SO_5$$

Lactic Acid. Propionic Acid Hydrated Lactic Peroxide.

$$2C_3H_6O_3 = 2C_3H_6O_2 + O_2 \qquad 2C_3H_6O_3 = C_3H_6O_2 + C_3H_6O_4$$

Succinic Acid. Hydrated Succinic Peroxide.

$$2C_4H_6O_4 = 2C_4H_6O_3 + O_2 \qquad 2C_4H_6O_4 = C_4H_6O_3 + C_4H_6O_5$$

Camphoric Anhydride. Camphoryl. Camphoric Peroxide.

$$2C_{10}H_{14}O_3 = 2C_{10}H_{14}O_2 + O_2 \qquad 2C_{10}H_{14}O_3 = C_{10}H_{14}O_2 + C_{10}H_{14}O_4$$

Camphoric Acid. Hydrated Camphoric Peroxide.

$$2C_{10}H_{16}O_4 = 2C_{10}H_{16}O_3 + O_2 \qquad 2C_{10}H_{16}O_4 = C_{10}H_{16}O_3 + C_{10}H_{16}O_5$$

The mode of transition from the classification of the equations to the classification of the substances is sufficiently obvious.

The analogies expressed in column I. are for the most part very generally admitted, yet not in all cases. But on what principle, may we ask, can those who admit the analogies which exist between water, acetic acid, the oxide of ethylene, carbonic acid and sulphuric acid, and between hydrogen, aldehyde, ethylene, carbonic oxide, and sulphurous acid, and express these analogies in the formulæ, $H_2O$, $C_2\underset{H}{H_{30}}O$, $C_2H_4''O$, $CO''O$, $SO_2''O$; $H_2$, $C_2H_3O\ H$, $C_2H_4''$, $CO''$, $SO_2''$, decline to admit the existence of similar analogies between water, sulphuric acid, and lactic acid, and between hydrogen, hydrated sulphurous acid, and propionic acid, or refuse to write the formulæ of these substances, thus:— $H_2O$, $H_2SO_3''O$, $C_3H_6O_2''O$; $H_2$, $H_2SO_3''$, $C_3H_6O_2''$.

An inspection of column II will render evident that peroxide of hydrogen and the organic peroxides are related to chlorine by analogies precisely the same in kind as those by which ethyl, olefiant gas, aldehyde, and the radicals of the organic acids are connected with hydrogen.

It is to be observed that the electronegative, like the electropositive radicals, are of two classes, monatomic and diatomic. The former class is represented in the system of elements by chlorine, as the monatomic hydrocarbons are represented by hydrogen. But no element is known analogous to the latter class, in the same sense as the metals barium and lead are analogous to ethylene. The nature of this distinction is seen from the following equations, from which it is apparent that the relations of the electronegative radicals to the electropositive element, hydrogen, are the same as those of the electropositive radicals to the electronegative element, chlorine. Thus we have in the monatomic group:—

$$K_2 + Cl_2 = 2KCl$$
$$C_2H_6 + Cl_2 = 2CH_3Cl,$$

to which correspond the equations,

$$Cl_2 + H_2 = 2HCl$$
$$H_2O_2 + H_2 = 2H_2O$$

Acetic Peroxide.

$$C_4H_6O_4 + H_2 = 2C_2H_4O_2$$

Benzoic Peroxide.

$$C_{14}H_{10}O_4 + H_2 = 2C_7H_6O_2,$$

and in the diatomic group,

$$Ba + Cl_2 = BaCl_2$$
$$C_2H_4 + Cl_2 = C_2H_4Cl_2,$$

to which correspond the equations,

Peroxide of Barium. Hydrate of Baryta.

$$BaO_2 + H_2 = BaH_2O_2$$

Camphoric Peroxide. Camphoric Acid.

$$C_{10}H_{14}O_4 + H_2 = C_{10}H_{16}O_4.$$

A parallel of the closest character may be drawn between chlorine and the organic peroxides of the first system.

1. In the mode of their formation :—

Thus we have—

$$4HCl + BaO_2 = BaCl_2 + Cl_2 + 2H_2O$$
$$2HCl + BaO_2 = BaCl_2 + H_2O_2$$

Benzoic Peroxide.

$$2C_7H_5OCl + BaO_2 = BaCl_2 + C_{14}H_{10}O_4$$

Acetate of Barium. Acetic Peroxide.

$$2C_2H_6O_3 + BaO_2 = BaC_4H_6O_4 + C_2H_6O_4.$$

2. In their oxidising action :—

$$Cl_2 + 2HKO + {}^*MnH_2O_2 = 2KCl + H_2O + MnH_2O_3$$
$$C_4H_6O_4 + 2HKO + MnH_2O_2 = 2KC_2H_3O_2 + H_2O + MnH_2O_3$$

3. In their action on ferrocyanide of potassium, and on the alkaline peroxides :—

$$Cl_2 + 2K_4FeN_6C_6{}^\dagger = 2KCl + K_6Fe_2N_{12}C_{12}$$
$$C_2H_6O_4 + 2K_4FeN_6C_6 = 2KC_2H_3O_2 + K_6Fe_2N_{12}C_{12}$$
$$Cl_2 + BaO_2 = BaCl_2 + O_2$$

Benzoic Peroxide. Benzoate of Barium.

$$C_{14}H_{10}O_4 + BaO_2 = BaC_{14}H_{10}O_4 + O_2$$

Benzoate of Potassium.

$$C_{14}H_{10}O_4 + K_2O_2 = 2KC_7H_5O_2 + O_2.$$

4. In effecting the decomposition of water and the alkalies :—

$$2Cl_2 + 2H_2O = 4HCl + O_2$$

Acetic Peroxide.

$$2C_4H_6O_4 + 2H_2O = 4C_2H_4O_2 + O_2$$

---

* Mn = 54

† Fe = 50.

$$2Cl_2 + 4HKO = 4KCl + 2H_2O + O_2$$

Benzoic Peroxide. Benzoate of Potassium.

$$2C_{14}H_{10}O_4 + 4HKO = 4KC_7H_5O_2 + 2H_2O + O_2.$$

5. In combining with hydrogen and the metals :—

$$Cl_2 + H_2 = 2HCl$$
$$C_4H_6O_4 + H_2 = 2C_2H_4O_2.$$

6. In their combinations with the hydrocarbons of the olefiant gas series. This reaction appears to have been realized by Carius in the case of propylene :—

$$Cl_2 + C_2H_4 = C_2H_4Cl_2$$

Glycol.

$$H_2O_2 + C_2H_4 = C_2H_4O_2$$

Propylic Glycol.

$$H_2O_2 + C_3H_6 = C_3H_6O_2.$$

It must be admitted that these analogies are of the most profound and real character, and that the organic peroxides resemble chlorine far more closely than does cyanogen, which is generally regarded as the representative electronegative radical.

With the diatomic peroxides all the same reactions may be effected as with the monatomic peroxides, but the equations which express these reactions are different in form ; and there is, as I have already observed, no known element which, strictly speaking, is analogous to these substances, unless fluorine be such, with regard to which little is known, but some of the combinations of which appear to indicate a diatomic character.

If we construct the equations which express the reactions of the anhydrous camphoric peroxide, we have—

Camphoric Peroxide. Camphoric Acid.

$$C_{10}H_{14}O_4 + H_2O_2 = C_{10}H_{16}O_4 + O_2$$

Hydrated Camphoric Acid.

$$C_{10}H_{14}O_4 + H_2 = C_{10}H_{16}O_4$$

Camphorate of Potassium.

$$C_{10}H_{14}O_4 + 2HKO + MnH_2O_2 = C_{10}H_{14}K_2O_4 + H_2O + MnH_2O_3$$

which differ from the preceding equations in the same manner as the equations which express the reactions of olefiant gas differ from those which express the corresponding reactions of hydrogen.

These ideas may be said to date almost from the discovery of chlorine. We know that, from the mode of formation of chlorine, from the evolution of oxygen by the action of chlorine upon water, and from its oxidizing properties, the illustrious Berthollet was led to the conclusion that chlorine contained oxygen, and was the oxide of hydrochloric acid. Again, the analogies of chlorine and the peroxide of hydrogen could not escape Laurent.* But, by a singular perversity, this chemist only seized the idea for the purpose of ridiculing it. Speaking of peroxide of hydrogen under the assumed name of *eurhyzen,* he pointed out some of the analogies of this body to chlorine, and considered that, by a *reductio ad absurdum,* he had shown the folly of the radical theory. Recently these analogies have been considered more seriously, and many chemists, Williamson, Kolbe, Laurent, Wurtz, Kekulé,† and, I may add, myself, pointed out some years ago, the constancy of the radical HO in chemical transformations, and the simple view of the relations of organic bodies which was afforded by regarding this body as a compound radical analogous to hydrogen.

However, these views stand in a much nearer relation to the celebrated binary theory of acids and salts, than to any other doctrine. Dulong, in 1816,‡ following the idea of Davy, appears to have been the first distinctly to regard the oxygenated acids as binary compounds, consisting, not of water and the anhydrous acids, but of hydrogen and compound radicals composed of the other constituents of the acids. Thus he regarded oxalic acid as the hydride of carbonic acid, $H_2 + CO_2$, and sulphuric acid as $H_2 + SO_4$.

A reality was given to this theory, which it had not before possessed, by the researches of Daniell § on the electrolysis of salts. This chemist observed that, in the electrolysis of a salt, besides an amount of oxygen and hydrogen equal to the oxygen and hydrogen simultaneously evolved in a voltameter placed in the circuit, or equivalent to the chlorine and the lead evolved in a voltameter containing fused chloride of lead, an equivalent of acid and of base was also formed; and that, if the positive and negative terminals of the battery were separated by a porous diaphragm, at the one pole appeared an equivalent of acid and an equivalent of oxygen, at the other an equivalent of hydrogen and an equivalent of base. Now, it was not to be imagined that the same amount of electricity which decomposed one equivalent of fused chloride of lead in the voltameter could decompose an equivalent of water, and also an equivalent of the salt in the decomposition cell,—that it could in the cell do double the work which was effected in the voltameter; and he explained the facts by the hypothesis that the salt, say sulphate of potash, was decomposed into an equivalent of potassium, and an equivalent of the radical $SO_4$, which he termed *oxysulphion.* The potassium decomposed the water, evolving hydrogen and forming potash. The radical $SO_4$, he considered to break up into $SO_3$, the anhydride which combined with water to form the hydrated acid, and oxygen, which was evolved.

---

* See "Chemical Method.," p. 293.

† See Kekulé Lehrbuch der organischen Chemis, vol. i, 736.

‡ See Kopp. Geschichte der Chemie, vol. iii, p. 21.

§ See Daniell's Chemical Philosophy, Ed. 1843, p. 434 and 532, and Phil. Trans., 1839.

The more exact account of this reaction, according to our present ideas, is to consider that similar reactions occur at the two terminals; that the potassium, the basylous radical, decomposes water, with evolution of hydrogen. $K_2 + 2H_2O = 2HKO + H_2$; and that the acid radical $SO_4$ also decomposes water, evolving oxygen: $2SO_4 + 2H_2O = 2H_2SO_4 + O_2$.

Now, the electrolysis of the organic salts is perfectly consistent with this view. Acetate of potassium, as we know, is decomposed, with formation, at the positive pole of the battery, of carbonic acid and methyl, and valerianate of potassium gives at the same pole carbonic acid and butyl. But these are precisely the products which we should expect to find from the decomposition of the peroxides of these radicals. Thus—

Acetic Peroxide.

$$C_4H_6O_4 = C_2H_6 + 2CO_2$$

Valerianic Peroxide.

$$C_{10}H_{18}O_4 = C_8H_{18} + 2CO_2.$$

But further, Kekulé* has recently shown that succinate of potassium is decomposed by the electric current, with formation of olefiant gas and carbonic acid, and fumaric acid, with formation of acetylene and carbonic acid. These would be the products of the decomposition of the succinic and fumaric peroxides respectively, thus:—

---

* See Bulletin de la Société Chimique de Paris, 1864, p. 243.

Succinic Peroxide.

$$C_4H_4O_4 = C_2H_4 + 2CO_2.$$

Fumaric Peroxide.

$$C_4H_2O_4 = C_2H_2 + 2CO_2.$$

In the electrolysis of oxalic acid, carbonic acid alone appears at the positive pole.

Oxalic Peroxide.

$$C_2O_4 = 2CO_2$$

It would certainly be very desirable, in confirmation of these views, to detect the peroxides at the positive pole of the battery, and it seems not improbable that this may be done. It is well known that, in the electrolysis of a strong solution of sulphuric acid, the oxygen and hydrogen do not appear in equivalent proportions, but that there is a very great deficiency of oxygen. Meidinger* has shown that, under certain modifications of the experiment, more than $\frac{5}{6}$ of the oxygen are retained in the fluid, which he found to possess the property of oxidising hydriodic acid. He attributes these phenomena to the formation of peroxide of hydrogen; but this substance is not formed. I have repeated his experiment and found that the liquid does not manifest the properties of peroxide of hydrogen in regard to chromic acid and permanganic acid. On the other hand, when it is warmed with a solution of indigo, the indigo is bleached; ferrocyanide of potassium also is oxidised by it. These are the properties of the peroxide of the acid, and it is probable that the peroxide of sulphuric acid, $H_2SO_5$, the analogue of the hydrated peroxide of camphoryl, $C_{10}H_{16}HO_5$, is the cause of these peculiar reactions.

The binary theory of salts was the great chemical generalization, which resulted from the discovery of chlorine. No idea in chemistry has been more fertile than this. In it was implicitly contained, and from it was developed, the doctrine of compound radicals. Here, for the first time, a just comparison was made of the compound and the element, and the identity of their chemical functions recognised. In it we may discern the germs of the theory of types. We are now familiar with such conceptions, but some thirty years since, the binary theory of salts was spoken of by the leading chemists of that day with profound, and yet with hesitating admiration, as introducing fundamental changes in chemical ideas. There was felt, however, to be one obstacle to its reception. It necessitated, or was considered to necessitate, the existence of numerous substances, which had never been formed.* This obstacle is now removed. The discovery of the organic peroxides supplies the necessary basis of fact to the speculations of Davy and Dulong; at length their ideas are realized. Here are the very electronegative radicals, the new, the compound chlorines, whose existence they surmised.

---

* Ann. Ch. Pharm, lxxxiv, 57 and 77.

It can hardly be believed, that this long train of analogies ends here. Other points of resemblance between the organic peroxides and chlorine, other properties which they possess in common, will surely be discovered. At any rate such analogies afford suggestions for experiment. Let us treat these substances as though they were chlorines. Is it not probable that they will combine with carbonic oxide, and with olefiant gas? May we not hope to effect by their agency the substitution for hydrogen, of the electro-negative compound radical?

## XXXIII.—*A Contribution to the History of the Oxides of Manganese.*

By W. Dittmar.

It has long been known that oxides of manganese, when heated to redness in air, either evolve or absorb oxygen, so as constantly to leave a residual oxide of the composition $Mn_3O_4$. Some years ago, Schneider found that when the ignition is made in pure oxygen, the residue consists of $Mn_2O_3$.†

This result differs from what might have been expected; for we do not know of any chemical action exerted by nitrogen on the oxides of manganese or on free oxygen, and, therefore, one might have thought that air would act simply like dilute oxygen, and produce the same oxide.

---

* See the interesting criticism of the binary theory by M. Dumas in his "Leçons sur la Philosophie Chimique," delivered in 1836, from which I cannot refrain from quoting the following passage:—"J'insiste sur ce raisonnement, car je ne trouve pas d'autres faits à opposer au système soutenu par Davy et M. Dulong: Ainsi la question n'est pas irrévocablement vidée. D'un moment à l'autre, il est possible que cette théorie se relève triomphante, appuyée par quelque découverte qui lui donnera une force nouvelle. Mais jusqu'à présent je suis d'avis qu'elle doit être repoussée, en raison de cette multitude innombrable d'êtres inconnus qu'elle suppose. Si seulement j'en voyais naître une partie . . . j'aurais moins de répugnance à croire à l'existence du reste."—*Leçons sur la Philosophie Chimique*, par M. Dumas, p. 292. Ed., Bruxelles, 1839.

† Poggendorff's Annalen, cvii, 605.

To explain the result of Schneider's experiment, we must suppose either that artificially made oxygen differs in some respects from that in the atmosphere, or what is more likely, that the proportion of oxygen in the residue depends on the *tension of the oxygen* in which the original oxide was heated, as well as on the temperature to which it was exposed.

Accepting this latter explanation, we say that, at a red heat, in presence of oxygen of the tension of one atmosphere, the oxide $Mn_2O_3$, being the most stable under these conditions, is formed, while at the same temperature, with oxygen of the tension of only one-fifth of an atmosphere, the oxide $Mn_3O_4$ is the most stable, and hence it is produced. This leads to the question,—What oxides will be formed when oxygen of intermediate tensions is employed? Will there be a continuous series of oxides corresponding to a continuous series of oxygen tensions under which they have been formed?

These questions seemed to me to merit an experimental investigation, and that the more, because the results of such an inquiry would be a small contribution to our as yet very imperfect knowledge of the laws which govern the influence of physical conditions on chemical reactions.

In a preliminary series of experiments, pure binoxide of manganese, prepared by heating the nitrate, was heated to dull redness in a combustion-tube, whilst in the first experiment, a current of nitrogen, in the second, one of air, and in the third, one of oxygen, was kept passing over it. After weighing the residual oxide, it was again heated under the same conditions as before, and then weighed a second time. Finally, by ignition in a current of hydrogen, it was reduced to protoxide, which was also weighed.

The following Table contains the results—

TABLE I.

| No. of Exp. | Gas employed. | Weight of the oxide after | | Weight of MnO | Composition of Oxide $= MnO_x$. |
|---|---|---|---|---|---|
| | | 1st heating = P. | 2nd heating = P′. | | |
| 1 | Nitrogen .. | 0·7984 grm. | 0·7971 | 0·7184 | from P; $x = 1{\cdot}494$<br>from P′; $x = 1{\cdot}486$ |
| 2 | Air ...... | 0·891 „ | 0·891 | 0·798 | $x = 1{\cdot}517$ |
| 3 | Oxygen .. | 1·084 „ | 1·084 | 0·969 | $x = 1{\cdot}527$ |

From these data it will be seen that in each of the three experiments, $Mn_2O_3$ was obtained. This fact led me to think that Schneider, in heating an oxide of manganese in pure oxygen, obtained the sesquioxide, only on account of his having performed his experiments at about the same temperature that I employed, at which air, and even nitrogen, gives the same result as oxygen.

The second series of experiments showed, however, that the oxide $Mn_2O_3$ *is* stable when heated in oxygen, even at a higher temperature than would suffice in presence of air to reduce it to $Mn_3O_4$. In this series of experiments, pure binoxide of manganese, in a porcelain or platinum boat, was placed within a porcelain tube, and the whole heated to bright redness for about an hour, while a current of dry nitrogen or oxygen, or a mixture of the two, was passing over it. The oxide was then analysed as before, by igniting in hydrogen and weighing the protoxide left. Most of the experiments were conducted under the ordinary atmospheric pressure, but in a few, the tension of the gas in which the $MnO_2$ was heated, was diminished below one atmosphere by con-

TABLE II.

| No. | Nature of atmosphere. | Tension* in atmospheres of. | | | Weight of Oxide of Manganese. | Weight of MnO obtained from it. | Composition of Oxide being MnOx. |
|---|---|---|---|---|---|---|---|
| | | V. | Θ. | N + O. | | | |
| 1 | Oxygen . . . . . . . . . . . . . . . . | 0 | 1 | 1 | ·9500 | 0·8191 | 1·527 |
| 2 | Nitrogen. . . . . . . . . . . . . . . . | 1 | 0 | 1 | 0 1269 | 0·3993 | 1·307 |
| 3 | Air . . . . . . . . . . . . . . . . . . . . | 0·79 | 0·21 | 1 | 0 7185 | 0·6935 | 1·352 |
| 4 | Equal vol. of air and oxygen | 0·40 | 0·60 | 1 | 0·6559 | 0·5879 | 1·513 |
| 5 | Nitrogen. . . . . . . . . . . . . . . . | 1 | 0 | 1 | 0·3912 | 0·3670 | 1·329 |
| 6 | Oxygen . . . . . . . . . . . . . . . . | 0 | 1 | 1 | 0·8738 | 0·7814 | 1·506 |
| 7 | Air . . . . . . . . . . . . . . . . . . . . | 0·79 | 0·21 | 1 | 0·6163 | 0 5672 | 1·384 |
| 8 | 1 vol. oxygen, 2 vol. air . . . | 0·53 | 0·17 | 1 | 0 7165 | 0·6687 | 1·516 |
| 9 | Vacuum of air . . . . . . . . . . . | 0·013 | 0·003 | 0·016 | 1·0256 | 0·9505 | 1·350 |
| 10a | 1 vol. of oxygen, 5 vol. of air . . . . . . . . . . . . | 0·66 | 0·34 | 1 | 0·7571 | 0·6821 | 1·488 |
| 10b | | | | | 0·9038 | 0·8098 | 1·515 |
| 11a | Mixture of oxygen and nitrogen, both artificially made . . . . . . | 0·81 | 0·19 | 1 | 0·6756 | 0·6265 | 1·348 |
| 11b | | | | | 0·3426 | 0·3180 | 1·343 |
| 12 | Oxygen of low tension . . . . | 0 | 0·17 | 0 17 | 0·9062 | 0·8412 | 1·343 |
| 13 | Oxygen of low tension . . . . | 0 | 0·027 | 0·027 | 0·6769 | 0·6292 | 1·336 |
| 14 | Oxygen of low tension . . . . | 0 | 0·16 | 0·16 | 0 6333 | 0·5876 | 1·315 |
| 15 | 15 vol. of air, 1 vol. of oxygen . . . . . . . . . . . | 0·74 | 0·26 | 1 | 0·8172 | 0·7362 | 1·488 |
| 16 | | 0·74 | 0 26 | 1 | 0·8658 | 0·7736 | 1·529 |

---

* The tensions given do not pretend to be more than rough approximations to the real values.

necting the exit-end of the porcelain tube with a large bell-jar, within which the pressure was diminished, and kept constant by means of an air-pump. The preceding Table gives the result of eighteen experiments carried out in this manner.

It will be seen that, in each of the experiments, the number of the equivalents of oxygen (O = 8), combined with one of manganese (Mn = 27·5), was very near either to 1½ or to 1⅓, that is to say, either $Mn_2O_3$, or $Mn_3O_4$ was produced, and *intermediate oxides were not formed.* These two oxides which were formed are easily distinguished, the sesquioxide being black, while the oxide, $Mn_3O_4$, is brown. In a few cases, a large quantity of the brown oxide was obtained, side by side, *but not mixed,* with a small quantity of the black sesquioxide; but the amount of the latter was never sufficiently great to make the composition of the whole, *as given in the table,* differ materially from $Mn_3O_4$. In all cases in which $Mn_3O_4$ was obtained, the partial tension of the oxygen lay between 0 and 0·21 atmospheres. As is stated in the Table, some of the experiments were made with nitrogen (Nos. 2 and 5), and some with air (Nos. 3, 7, 9) of different pressures. Others were performed with oxygen of low tension (Nos. 12, 13, 14), or with a mixture of artificial oxygen and nitrogen (Nos. 11a and 11b). In those experiments which gave $Mn_2O_3$, the tension of the oxygen lay between 0·26 and 1 atmosphere. Oxygen tensions between 0·21 and 0·26 atmospheres did not occur in this series; still we can assert with a high degree of probability, that the function expressing the relation between the *composition* of an oxide of manganese, formed at a bright red heat in an atmosphere of oxygen, and the tension of that oxygen, is *discontinuous,* or that $Mn_2O_3$ is formed whenever the tension exceeds, and $Mn_3O_4$, whenever it is below, a *certain definite limit.*

To find out whether there is really such a limit, and if so to determine its position, I undertook a third series of experiments, which, for the sake of comparison, were made as uniform as possible. In each experiment the bioxide of manganese was placed in a platinum boat, which was itself placed on a strip of platinum foil, and by means of this introduced into the porcelain tube. (The same tube and boat were used in all the experiments). The tube was subjected to the strongest heat of a Hofmann's gas furnace for about half an hour, while a current of oxygen and nitrogen, mixed in exactly known proportions, was sent through it. The boat was then quickly withdrawn from the tube and allowed to cool. As this required only a very few minutes, no appreciable quantity of $Mn_2O_3$ could be formed at the temperatures conducive to its formation. The oxide was then weighed and analysed by determining the amount of $Mn_3O_4$ which it gave when ignited in a current of air partially deprived of its oxygen. The mixtures of oxygen and nitrogen which I employed were made from air and oxygen.

The air was collected in a glass gasometer over water, which had been previously saturated with air at the temperature of the laboratory. Its volume was determined by measuring the water which it displaced, and its temperature was assumed to be that indicated by a thermometer hung up close to the gasometer, while its tension was made equal to that of the surrounding atmosphere. In some experiments, the temperature was taken more carefully by plunging the whole gasometer into a water-bath of a constant known temperature, until equilibrium of temperature was established. The oxygen was measured out in a small glass gasometer, which was entirely immersed in a water-bath of known and constant temperature. The tension of the gas was in most cases made equal to that of the atmosphere, by originally collecting it under a higher pressure, and after establishing the desired temperature, allowing the excess of the gas to escape through a layer of water from 1 to 2 mm high. Lastly, the oxygen was transferred to the air-gasometer by displacing it with water, through which oxygen had been previously passed for some time. The gaseous mixture was displaced by water previously saturated with air, and before entering the porcelain tube, it passed first through a soda-lime, and then through a chloride of calcium tube, to free it from carbonic acid and water.

The volume of the oxygen formed in all cases only about one-twentieth of that of the air, and hence any error in measuring the proportions of oxygen and air, gave rise to a comparatively small error in estimating the proportion of oxygen in the mixture. For the same reason, the absorptiometric exchange between the gaseous mixture and the water could not change the composition of the former to any appreciable extent.

In determining the composition of the mixtures, one volume of air was assumed to contain 0·2093 vol. of oxygen. The following experiments were carried out in the manner described:

## TABLE III.

The following abbreviations are used in the sequel :—

*V* for volume in litres, and *P* for pressure in inches of mercury of a gas.

*t* for temperature in centigrade degrees.

*Q* for volumes of oxygen in 100 vols. of gaseous moisture.

*p* for partial pressure of the oxygen prevailing during the experiment.

*B* for height of barometer in inches.

*W* for weight in grammes.

### EXPERIMENT 17.

$$\left.\begin{array}{ll} \textit{Air.}^{*} & V = 10{\cdot}90 \\ \textit{Oxygen.}^{*} & V = \phantom{1}0{\cdot}50 \end{array}\right\} \begin{array}{l} P \text{ the same in both cases.} \\ t \text{ not observed.} \end{array}$$

As the temperatures of both gases were about the same, *Q* is approximately = 24·4.

*B* during ignition = 29·68; hence *p* = 7·24.

The greater part of the oxide obtained was brown, a small portion of it black.

*W* of oxide obtained = 1·0716.

*W* after reduction to $Mn_3O_4$ = 1·0683.

Therefore its composition:

$$\left.\begin{array}{lr} Mn_3O_4 \;\; .. \qquad .. & 0{\cdot}9739 \\ Mn_2O_3 \;\; .. \qquad .. & 0{\cdot}0977 \end{array}\right\} \text{grammes.}$$

### EXPERIMENT 18.

*Air.* $V = 10{\cdot}91$; $t = 12{\cdot}2$, $P$ = that of atmosphere = *B*.

*Oxygen.* $V = 0{\cdot}35$; $t = 9{\cdot}5$, $P = B + 1{\cdot}2$.

Hence *Q* = 23·5.

*B* during ignition was not observed; taking it = 30, *p* becomes = 7·05.

*W* of oxide obtained = 1·8884.

*W* after reduction to $Mn_3O_4$ was = 1·8880.

Loss of oxygen = 0·0004, corresponding to 0·0118 of $Mn_2O_3$; the rest consisted of $Mn_3O_4$.

---

* In this as well as in the following experiments, the *V* and *P* given for air and oxygen refer to the moist gases.

### EXPERIMENT 19.

*Air.* $V = 10{\cdot}91$; $t = 13{\cdot}3$; $P = 29{\cdot}92$.
*Oxygen.* $V = 0{\cdot}54$; $t = 10{\cdot}3$; $P = 30{\cdot}5$.
Hence $Q = 24{\cdot}7$; $B$ during ignition $= 29{\cdot}84$; hence $p = 7{\cdot}38$.
Weight of oxide obtained, 0·9030.
After reduction to $Mn_3O_4$, 0·8626.
Hence its composition: MnO 1·557; *i.e.*, $Mn_2O_3$.

### EXPERIMENT 20.

$$\left.\begin{array}{ll}\textit{Air.} & V = 12{\cdot}77;\ t = 10{\cdot}5\\ \textit{Oxygen.} & V = 0{\cdot}490;\ t = 83{\cdot}\end{array}\right\}\ P \text{ the same in both cases.}$$

Hence $Q = 23{\cdot}9$, and as $B$ during ignition $= 29{\cdot}46$, we have $p = 7{\cdot}04$.

Most of the oxide obtained was brown, a small part was black.

$W$ of oxide $= 0{\cdot}8222$.

After reduction to $Mn_3O_4$ it was 0·8217.

The 0·0005 of oxygen lost correspond to 0·0148 of $Mn_2O_3$; the rest, 0·8074, consisted of $Mn_3O_4$.

### EXPERIMENT 21.

$$\left.\begin{array}{ll}\textit{Air.} & V = 11{\cdot}41;\ t = 15{\cdot}8\\ \textit{Oxygen.} & V = 0{\cdot}503;\ t = 12{\cdot}2\end{array}\right\}\ P \text{ the same in both cases.}$$

Hence $Q = 24{\cdot}3$, and as $B$ during ignition $= 21{\cdot}52$, therefore, $p = 7{\cdot}17$.

Most of the oxide was black, a small portion only being brown.

$W$ of oxide $= 1{\cdot}1745$.

After reduction to $Mn_3O_4$ it was 1·1417.

Hence composition:

$$Mn_3O_4 = 0{\cdot}2035.$$
$$Mn_2O_3 = 0{\cdot}9710.$$

### EXPERIMENT 22.

$$\left.\begin{array}{ll}\textit{Air.} & V = 11{\cdot}90\\ \textit{Oxygen.} & V = 0{\cdot}499\end{array}\right\}\ P \text{ and } t \text{ exactly the same in both cases.}$$

Hence $Q = 24{\cdot}1$, and as $B$ during ignition $= 29{\cdot}32$, therefore p $= 7{\cdot}07$.

$W$ of oxide obtained 0·8648.

After reduction to $Mn_3O_4$ it was 0·8643.

The 0·0005 of oxygen lost correspond to 0·0148, of $Mn_2O_3$, the rest consisted of $Mn_3O_4$.

### EXPERIMENT 23.

$$\left.\begin{array}{ll} \textit{Air} & V = 11{\cdot}7 \\ \textit{Oxygen} & V = 0{\cdot}499 \end{array}\right\} t \text{ and } P \text{ the same in both cases.}$$

Hence $Q = 24{\cdot}2$, and as $B$ during ignition $= 29{\cdot}54$, $p = 7{\cdot}14$.
$W$ of oxide = 0·6513.
After reduction to $Mn_3O_4 = 0{\cdot}6281$.
Therefore composition, $MnO_{1{\cdot}510}$ *i.e.* $Mn_2O_3$.

### EXPERIMENT 24.

$$\left.\begin{array}{ll} \textit{Air} & V = 14{\cdot}54 \\ \textit{Oxygen} & V = 0{\cdot}502 \end{array}\right\} P \text{ and } t \text{ the same in both cases.}$$

This mixture was employed three times under different pressures.

*Experiment a.*—The tension of the mixture was made greater than that of the atmosphere by forcing it, after coming out of the porcelain-tube, through a layer of water, 4·5 inches deep. $B$ during ignition = 29.96, hence $p = 7{\cdot}14$.

This time the binoxide of manganese, previous to being heated in the mixture of oxygen and nitrogen, was converted into $Mn_2O_3$ by ignition in pure oxygen.

*Experiment b.*—The oxide obtained in experiment *a* was heated in the same gas as before, but this time without increasing its pressure beyond that of the atmosphere $B = 29{\cdot}95$, therefore $p = 7{\cdot}06$.

*Experiment c.*—The oxide obtained in experiment *b* was heated in the same mixture of N and O as before; the tension of the latter, however, was brought down below that of the atmosphere by sending it from the porcelain tube into a large bolt-head, within which the pressure was diminished and kept constant by sucking. The difference between this pressure and that of the atmosphere was measured by means of a water-manometer. The height of the latter was kept as near as possible to 5·5 inches. $B = 29{\cdot}9$; hence $p = 6{\cdot}95$.

At last the oxide from experiment *c* was reduced to $Mn_3O_4$ in the ordinary way.

The composition of the oxides obtained in these three experiments is given in the following table :—

Weight of $Mn_2O_3$ employed = 1·1852.

| Exp. | *p.* | *W.* of Oxide. | Composition. |
|---|---|---|---|
| a. | 7·14 | 1·1842 | $Mn_{1\cdot503}$. |
| b. | 7·06 | 1·1842 | $Mn_{1\cdot503}$. |
| c. | 6·95 | 1·1469 | 1·0463 of $Mn_3O_4$.* and<br>0·1006 of $Mn_2O_3$. |
| After reduction to $Mn_3O_4$ | | 1·1435 | $Mn_3O_4$. |

It is seen that, under the oxygen tension of 7·06, $Mn_2O_3$ was not decomposed, while under the oxygen tension of 6·95 it was for the most part reduced to $Mn_3O_4$. Under the conditions prevailing in experiment 24, therefore, the point of discontinuity above spoken of seems to correspond very nearly to an oxygen-pressure of 6·95 inches.

### EXPERIMENT 25.

*Air.* $V = 14{\cdot}00$ } $t$ and $P$ of both gases the same.
*Oxygen.* $V = 0{\cdot}407$ }

The same mixture was employed under two different pressures.

*In Experiment a,* the tension of the mixture of nitrogen and oxygen was made to exceed that of the atmosphere by 6·8 inches of water-pressure. $B = 30{\cdot}03$, therefore $p = 7{\cdot}07$.

*Experiment b.* Pressure of gaseous mixture $= B = 30{\cdot}05$, hence $p = 6{\cdot}96$. Under this pressure, the oxide obtained in experiment *a* was ignited. The composition of the oxides will be given below.

### EXPERIMENT 26.

*Air.* $V = 14{\cdot}02$ } $P$ and $t$ the same in both cases.
*Oxygen.* $V = 0{\cdot}408$ }

*Experiment a.* In this mixture the oxide obtained in experiment 25 *b*, was heated. During the ignition $B = 30{\cdot}02$, therefore $p = 6{\cdot}95$.

*Experiment b.* 11·26 litres of the same mixture of nitrogen and oxygen as was used in experiment *a*, of the temperature of 14° C, were mixed with 1·00 litre of air of 8° C. $P$ of both gases the same. In this mixture the oxide obtained in experiment *a* was ignited. B, during the ignition, 30·04, hence $p = 6{\cdot}90$.

*Experiment c.* 8·75 litres, at 11°C., of the same mixture of nitrogen and oxygen as was used in experiment *b*, were mixed with 0·50 litres (at 8°) of air. *P* of both gases was the same. In this mixture, the oxide obtained in experiment *b* was heated. *B* during ignition = 30·05, therefore *p* = 6.87.

---

* A small portion of the oxide was black; the greater part was brown.

*Experiment d.*—The oxide obtained in experiment *c* was again ignited in the same mixture of nitrogen and oxygen *B* = 30·03, hence *p* = 6·87.

*Experiment e.*—The oxide obtained in *d* was reduced to $Mn_3O_4$.

COMPOSITION OF OXIDES OBTAINED IN EXPERIMENTS 25 AND 26.

| Exp. | *P.* | *W.* of oxide. | Composition. |
|---|---|---|---|
| 25a | 7·07 | 0 7982 | $MnO_{1\cdot505}$ |
| 25b | 6 96 | 0 7982 | $MnO_{1\cdot505}$ |
| 26a | 6 95 | 0 7953 | 0 0829 of $Mn_3O_4$<br>0 7124 of $Mn_2O_3$ |
| 26b | 6 90 | 0·7982 | $MnO_{1\,505}$ |
| 26c | 6·87 | not determined | Mixture of brown and black oxide. |
| 26d | 6 87 | 0 7745 | 0 1184 of $Mn_2O_3$<br>0 6561 of $Mn_3O_4$ |
| 26e | | 0 7705 | $Mn_3O_4$ |

In order to define approximately the range of temperatures within which the experiments of this series had been performed, a piece of aluminum and also a piece of pure silver were placed into the porcelain tube, and heated in the same manner as had been the case with the oxide of manganese. Twenty minutes after the tube had become thoroughly heated, the aluminum was found to be fused, but not the silver.

We see that sometimes pure $Mn_2O_3$, sometimes pure $Mn_3O_4$ was formed, while in some cases both were obtained, side by side, not mixed; one of them, however, always greatly predominated in quantity.

$Mn_2O_3$ was formed alone or predominated in experiments:

| | 19 | 21 | 24a | 23 | 25a | 24b | 25b | 26b |
|---|---|---|---|---|---|---|---|---|
| *P* being respectively | 7 38 | 7·17 | 7·14 | 7·14 | 7·07 | 7·06 | 6·96 | 6·90 |

$Mn_3O_4$ was formed alone or predominated in experiments.

| | 26d | 24c | 20 | 22 |
|---|---|---|---|---|
| *P* being | 6·87 | 6·95 | 7·04 | 7·07[*] |

---

[*] Experiment 18 is not mentioned here, because in it the barometer was not observed during the ignition; also experiment 17 is omitted, because the high value of *P* deduced from it, makes me suspect some error committed in making the synthesis of the gaseous mixture.

These results seem to confirm the conclusions drawn from the second series of experiments. Experiments 24 *b* and 24 *c*, and also 26 *b* and 26 *d*, clearly show that, at a certain temperature, and in a certain atmosphere of nitrogen and oxygen, $Mn_2O_3$ will be stable, while a slight diminution in the tension of the oxygen, the other conditions remaining the same, will cause its reduction to $Mn_3O_4$. The exact value of the limiting tension of the oxygen below which $Mn_3O_4$, and above which $Mn_2O_3$ is formed, depends, no doubt, on the temperature to which the oxide of manganese is exposed. If we suppose that the function expressing this dependency is a *continuous one*, the apparently anomalous result of the third series of experiments, viz., that at oxygen-tensions contained between 6·60 and 7·07, either of the two oxides may be formed under *apparently* the same conditions, may be explained.

I cannot conclude without expressing my best thanks to Mr. Francis Jones, for his valuable assistance during the earlier part of this investigation.

University Laboratory, Edinburgh.

## XXXIV.—*On the Application of the Optical Properties of Bodies to the Detection and Discrimination of Organic Substances.*

By G. G. Stokes, M.A., D.C.L., Sec. R.S., Lucasian Professor of Mathematics in the University of Cambridge.

(A Discourse delivered before the Fellows of the Chemical Society, June 2nd, 1864.)

The optical properties of bodies, properly speaking, include every phenomenon in which ponderable matter is related to light by virtue of its molecular constitution, and not merely of its external form. Many of these, however, are of no use in helping us to follow a particular substance through mixtures or solutions containing it, though they may be useful as additional characters of substances which have been obtained in a state of isolation. Take for example refractive power. The refractive power of a pure substance, like its specific gravity, is one of the characters, the assemblage of which serves to distinguish it from other bodies; but as all bodies in nature refract light, solvents and body dissolved alike, though not to the same extent, the observation of the refractive power of a mixture would not help us in disentangling its constituents. The same may be said of dispersive power.

Circular polarization again belongs to the same class of properties; though from the fact that all inorganic, and a number of organic solvents are destitute of it, it is sometimes employed to trace a substance, but of course only in those cases in which we know or may presume that there is but one substance present which possesses the property in any marked degree.

If we exclude the emission of definite rays by flames and electric discharges, which is made known by spectral analysis, and which, though most valuable for the detection of elementary bodies, is of little or no avail for even the simplest and most stable compounds, and cannot of course be applied to organic analysis, there remain three phenomena in which bodies are related to light in a manner varying from one ray to another, not in a gradual, regular way like the refractive index, but in a way depending on something in the molecular constitution of the particular body in question, and changing sometimes in an apparently capricious way from one ray to another. These are (1) absorption, (2) fluorescence, (3) coloured reflexion.

I. The colour of substances has long been used as an important character; thus for example it is a character of the salts of oxide of copper, to yield in general blue solutions. In all cases in which colour is presented to us, we must, in considering the physical cause of the phenomenon, revert, in the first instance, to Newton's discovery of the compound nature of white light, and inquire how it comes to pass, that the homogeneous constituents of white light are presented to us in different proportions from those in which they occur in white light itself. Now, if a coloured solution be examined in homogeneous light of any kind, *i. e.*, light of definite refrangibility, it is found that the transmitted light, retaining all the properties of the incident light,* becomes feebler and feebler, as the thickness of the stratum through which it passes is increased. A portion of the incident light continually disappears as the rays traverse the solution, and is said to be *absorbed.* The incident light being by hypothesis homogenous, and the quantity of light which is absorbed in passing across a given stratum being, as experiment shows, proportional to the quantity which falls upon it, it readily follows, that the intensity of the light which escapes absorption decreases in geometrical progression, as the length of path of the rays within the solution increases in arithmetical. The rate of absorption changes in general from one set of homogeneous rays to another. For one part of the spectrum, the absorption produced by the solution may be very powerful, for another part very weak, while for another part again the solution may be sensibly transparent like water.

---

* Sir David Brewster indeed conceived that he had succeeded in analyzing by absorption light which was homogeneous as regards refrangibility. But though the direct judgment of the senses, *when the experiment is made in Sir David Brewster's manner*, is in accordance with his statement, as might be expected from his well known accuracy, the inference that a real analysis has taken place may be considered to have been disproved by subsequent researches.

To determine the absolute rate of absorption for homogeneous light of a given kind would be useless, unless the body to be examined were isolated; for not only would foreign substances present contribute to the observed absorption, unless, indeed, they happened to be perfectly transparent with respect to the part of the spectrum selected, but even in an otherwise colourless solution, it would be neccessary to estimate the quantity of substance present, since the rate of absorption would depend on the strength of the solution. Hence, *absolute* absorbing power is of no more avail for our purpose than refractive power.

But the *relative* absorption of different parts of the spectrum is what may be observed at a glance (of course, qualitatively only, not quantitatively); it is in general independent of the degree of dilution of the solution, the solvents being supposed colourless, and *when the substance to be observed has in this respect well marked characters,* may be observed to a very great extent independently of coloured impurities, even though they may be sufficient to change the colour very greatly.

For this purpose, nothing more is required than to form in any manner a pure spectrum, and interpose the coloured solution anywhere in the path of the rays forming it. The simplest mode of obtaining a pure spectrum, when we have no occasion to place objects in it, is to view a slit held against a luminous background, through a prism applied to the eye. Hence the following simple arrangement may be adopted.

A small prism is to be chosen, which may be made of rather dense flint glass ground to an angle of about 60°, and need not be larger than is sufficient just to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and of laying it down on an end, so as not to scratch or dirty the faces. This forms the only apparatus required beyond what the observer may readily make for himself. The slit may conveniently be made by taking a board 6 inches square, or a little longer in a horizontal direction, making an oblong aperture in it in a vertical direction, and adapting to the aperture two pieces of thin metal to form clean cheeks to the slit. One of the metal pieces should be moveable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that in scrutinizing one part after another it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. The use of a prism in this way is at the first moment a little puzzling, but soon becomes perfectly easy. To observe the absorption-spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye; but for actual work this is an unnecessary luxury. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding to a thickness of the solution, which increases in a continuous manner from the edge of the wedge, where it vanishes.

In many cases nothing is observed, beyond a general absorption of one or other end of the spectrum, or of its middle part, and the prism gives little information beyond what is got by the eye, by observing the *succession of colours* produced by different thicknesses of the liquid. And here it may be remarked in passing, with reference to the description of pure substances, that in specifying only one colour, that corresponding to a considerable thickness, as is commonly done by chemists, the peculiar features of the absorption are left almost wholly undescribed. Thus of two solutions, one might be pink when dilute, passing on to red with increase of strength or thickness, another yellow, passing through orange to red. These would commonly be described as red, yet the series of tints indicates an utter difference in the mode of absorption, the middle of the spectrum in the one case, and the most refrangible end in the other, being the most powerfully attacked.

But in some cases, especially with substances of intense colorific power, the mode of absorption is eminently characteristic. Two or more dark bands are seen in the spectrum, indicating maxima of absorption; and the positions of these bands, their relative intensity, and their other features, form altogether a series of characters the distinctive nature of which is such as those who have neglected the use of the prism have little conception of. They render it perfectly easy in many cases to follow a particular substance among a host of impurities. For each coloured substance produces its own absorption, independently of the others (supposing the substances do not chemically react on each other), so that, unless the part of the spectrum in which the distinctive bands, or most of them, occur, is wholly absorbed by the impurities, the presence of the substance can still be recognised. Such a complete obliteration is the less likely to occur, for this reason, that when the characters of the solution are so strongly marked, it almost always happens that a comparatively small quantity of the substance suffices to produce the effect, and the solution must consequently be so much diluted that the effect of the impurities comparatively disappears.

Nor is this all. When a substance exhibits marked characters of one kind in one solvent, it often happens that it shows different and no less marked characters in a solvent of a different nature. Not only does this furnish additional characters by which the substance can be distinguished from others, but it is valuable for following the substance when involved in impurities; for the nature of the impurities may be such as to mask the substance in one solvent and not in another. This is especially the case where one solvent is alkaline and the other acid; but differences are sometimes observed even with two neutral solvents.

To illustrate these principles, we may refer to the colouring matters of madder. Alizarin and purpurin both yield highly distinctive spectra, the former, however, only in the case of solutions containing caustic alkali,* whereas most solutions, of the latter are highly distinctive. Madder itself contains, either directly or as the result of decomposition, a number of substances which in alkaline solution absorb that part of the spectrum in which the distinctive bands of purpurin occur. Hence, in a mixture obtained from madder, and containing, we will suppose, purpurin in comparatively small quantity, the presence of purpurin would be masked by the other substances *in an alkaline solution*. But in ether or acidulated alcohol, the other substances yield spectra showing nothing particular, and interfering comparatively little with the distinctive bands of purpurin; while in an alum-liquor solution made by boiling, not only are the purpurin-bands, which in this solvent occur at a lower refrangibility than with ether, more effectually separated from the absorption produced by the associated substances, but those substances themselves are also in good measure excluded.

For an example of the necessity of attending to the nature of the solvent, even in the case of different neutral solvents, we may refer to a yellow substance which is one of the constituents of the green colouring matter of leaves. The alcoholic solution of this substance exhibits two characteristic bands of absorption, the first of which is situated immediately adjacent to the line F on the more refrangible side. The solution in bisulphide of carbon exhibits two similar bands, but much less refrangible, the line F now nearly bisecting the bright interval between the first and second dark bands. The substance is very easily decomposed by acids, and even by acid salts, yielding a product of decomposition which, in alcoholic solution, exhibits two bands of absorption like the parent substance, but a good deal more refrangible. There is the same change of position as in the former case, in passing from emitted by a solution becomes a character of importance. This tint, it must be remembered, is that of the light *as emitted*, not as *subsequently modified* by absorption on the part of the solution, in case the solution be sensibly coloured, and some precautions are required in order to observe it correctly.* The fluorescence observed in solutions from the barks of the horse-chestnut, ash, &c., was formerly attributed indiscriminately to the presence of æsculin, whereas a purified solution from the bark of the horse-chestnut exhibits a fluorescence very sensibly different from that of æsculin, which observation alone would suffice to show that the bark must contain some other fluorescent substance besides æsculin.

---

* On boiling with an alkaline carbonate the same spectrum is obtained, but not perfectly developed. An alcoholic solution with a little caustic potash introduced gives it in perfection.

As in the case of absorption, the nature of the solvent must be attended to. The colour of the fluorescent light is liable to change, not merely in passing from an alkaline to a neutral or acid solution, but even occasionally in passing from one neutral solvent to another. The lecturer has received from Dr. Müller a specimen of a substance which in water exhibits a *green*, but in ether a *blue* fluorescence.

The composition of fluorescent light, as revealed by the prism, occasionally presents peculiarities, but in such cases they are found to be connected with peculiarities in the mode of absorption, so that the two are not to be regarded as *independent* characters of a substance; and as the peculiarities in the absorption are, as a general rule, the more easily observed, it is only rarely that the analysis of the fluorescent light is of much use.

The distribution of fluorescence in the spectrum often affords valuable information, but its observation is not of that perfectly simple character, requiring hardly any apparatus, that constitutes one great advantage, for chemical application, of the observation of absorption or of the tint of fluorescent light. The observation is restricted to times when the sun is shining pretty steadily (unless the observer has recourse to electric light, or at least lime-light); it is requisite to reflect the sun's light horizontally, without which the observation would be most troublesome; and unless the reflexion be made by the mirror of a heliostat, the continual change in the direction of the reflected light is most inconvenient. It is requisite to use at least one good prism, better two or three, which must be of tolerable size, in order to have light of sufficient intensity, and the prisms must be combined with a lens, which need not however be achromatic. Hence these observations are not, like the former, adapted to the daily use of every chemist.

---

* See Quarterly Journal of the Chemical Society, vol. xi, p. 19.

It has already been stated, as the result of experience, that the colour of the fluorescent light of a single substance is constant throughout the spectrum, or very nearly so. If, therefore, on examining a solution in a pure spectrum thus formed by projection, we find the fluorescence taking a fresh start *with a different colour*, we may be almost certain that we have to do with a mixture of two different fluorescent substances, the presence of which is thus revealed without any chemical process. If, however, the fluorescence of two fluorescent substances, which may be mixed together, begins at nearly the same point in the spectrum (as commonly happens when there is merely a slight difference of tint in the colour of the fluorescent light of the two substances), the coexistence of the two substances may escape detection when the mixed solution is merely examined in a pure spectrum; and in such cases a combination of processes of fractional separation with the easy observation of the tint of the fluorescent light is more searching. This is the case, for instance, with the mixture of æsculin and fraxin contained in a solution from the bark of the horse-chestnut.

Experience has also indicated a most intimate connexion between the spectral distribution of fluorescence and that of opacity in the case of solutions of pure substances. There are, indeed, theoretical reasons for regarding it as not improbable that instances may yet be found in which absorption, unaccompanied by fluorescence, takes place, in the case of solutions of fluorescent substances, in that part of the visible spectrum which is less refrangible than the point at which the fluorescence commences, but no such instance has yet been observed. Hence from the distribution of the fluorescence, we may infer the character of the absorption belonging to the fluorescent body. For this purpose it is best to make the solution extremely dilute, when any bands of absorption will have their positions indicated by beams of fluorescent light, while in the intermediate parts of relatively great transparency, the fluorescence, in the case of such weak solutions, is almost insensible.

As the occurrence of a decided difference of colour in the fluorescent light seen at two different parts of the spectrum implies, almost to a certainty, the presence of two different fluorescent substances, so, conversely, the exhibition of the same colour is an argument in favour of the identity of the substance producing the fluorescence at the two parts. We cannot indeed say that there may not be two substances present, the fluorescence of which commences at nearly the same part of the spectrum; but assuredly, two different substances, the fluorescence of which commenced at two widely different parts of the spectrum, would reveal themselves by the difference of colour. For experience shows that the refrangibility of the light emitted, at any part of the incident spectrum, by the solution of a pure substance, extends nearly up to that of the point of the incident spectrum at which the fluorescence commences, but not much beyond; and though, in passing from one pure substance to another, variations do occur in the relative brightness of the rays of less refrangibility which compose the fluorescent light, yet, on the whole, there is so close a connexion between the colour of the fluorescent light and the refrangibility of the rays by which the fluorescence is first produced, that no great variation in the one is compatible with constancy or a mere trifling variation in the other.

For an example of the application of these principles, we may refer to the green colouring matter of leaves. The alcoholic solution of this substance exhibits a lively fluorescence of a blood-red colour, and shows also a certain system of bands of absorption. Different chemists in different ways have obtained from it a yellow substance, and M. Frémy, having obtained a yellow substance by the aid of merely neutral reagents, has proved that such a substance pre-exists. The yellow solution was obtained by him in the attempt to divide the green colouring matter into a yellow and a blue; but, by using neutral reagents only, he did not get further in the direction of blue than a green of a bluer shade than at first, which he supposed to be due to the imperfection of the modes of separation. He conceived, however, that he had attained his object by dissolving chlorophyll in a mechanical mixture of ether and hydrochloric acid, the acid stratum, when the fluids separated after agitation, exhibiting a blue colour.

Now, when an alcoholic solution of chlorophyll is examined in a pure spectrum formed by sunlight, in the part of the spectrum extending from the extreme red to the junction of the green and blue the fluorescence exhibits remarkable fluctuations of intensity, corresponding precisely to the bands of absorption in the transmitted light. The red fluorescence is extremely lively in nearly the whole of the blue and in the violet. This proves that the main absorption of these colours cannot be due to the yellow body; for the yellow substance would be either non-fluorescent, or its fluorescence would be of some shade of green or yellow. On the former supposition, the fluorescence of the chlorophyll solution in the blue and violet would be dull, and on the latter would be of some colour different from blood-red, unless the main absorption of that part of the spectrum were due to the substance producing the red fluorescence. In fact, when the yellow body is nearly isolated, it exhibits two characteristic bands of absorption in the blue, to which no fluorescence corresponds, which demonstrates that the slight red fluorescence which the solution may still exhibit is due to the remaining impurity. Hence, if the yellow body were wholly eliminated from chlorophyll, the residue, containing the substance showing the red fluorescence, would still powerfully absorb the blue and violet, and therefore could not be blue, but only a bluer green; so that in seeking to separate chlorophyll into a blue and a yellow substance, M. Frémy was aiming at an impossibility. His phyllocyanin is, in fact, a product of decomposition, and is not blue at all, but merely dissolves in certain acids with a blue colour. It may be mentioned in passing, that the green fluorescent residue is still a mixture, consisting of two different substances, both green, and both exhibiting a red fluorescence.

III. The instances in which substances appear coloured by reflexion are comparatively rare. It is very common in chemical descriptions to read of a solution appearing of such a colour by transmitted, and such a colour by reflected light. In many cases, this is a positive mistake, and the colour described as due to reflexion is really due to transmission. A chemist views a solution contained in a test tube by transmission, and then by reflexion; and seeing, perhaps, some perfectly different colour in the latter case, describes it as the colour of the solution by reflexion, whereas it is merely the colour by transmission due to a greater thickness, the light having been reflected at the back or bottom of the test tube, and so having twice passed through the solution. In other cases the colour described as due to reflexion really arises from fluorescence; and though the statement may be true in the sense intended, it seems objectionable to apply the term *reflexion* to a process so utterly different. It is only in the case of metals, such as gold and copper, and of certain other substances such as murexide, platocyanide of magnesium, &c., that colour is really seen as the result of reflexion.

When this takes place in the case of non-metallic substances, they are found to be endowed, for the colours so reflected, with an intense opacity, comparable with that of metals; while for other parts of the spectrum they may be comparatively transparent, and these parts they reflect with an energy comparable to that of a vitreous substance only. The variations of absorbing power in passing from one part of the spectrum to another, and consequently the variations in reflecting energy, are frequently much more considerable, and accordingly the colour by reflexion is much richer than in the case of metals.

An excellent example of the intimate connexion between metallic reflexion and intense absorption is afforded by crystals of permanganate of potash. These crystals exhibit a green metallic reflexion, and when crushed yield a powder of an intense purple colour by transmitted light. The colour is too intense for spectral analysis, but the solution has a similar colour, merely less intense as corresponds with its smaller concentration, and the analysis of the light transmitted by the solution presents no difficulty. The green is quickly absorbed, but when the solution is sufficiently dilute, five eminently characteristic bands of absorption are seen in that part of the spectrum. A sixth band comes out with a greater thickness or else strength of solution, but even the fifth is somewhat less strong than the others. When the light reflected from a crystal is analysed, four bright bands are seen standing out on a generally luminous ground of inferior brightness. These bright bands correspond in position with the principal *dark* bands in the light transmitted by the solution, and therefore, it may be presumed, by the crystals themselves. When the angle of incidence has a suitable value, and the reflected light is analysed by a Nicol's prism, with its principal plane in the plane of incidence, and then by a common prism, the spectrum is reduced to these four bright bands. A fifth bright band could perhaps be made out, in the case of a fine crystal with a fresh surface. Under the circumstances described, the Nicol's prism would extinguish the light reflected from a vitreous substance, and transmit much of that reflected from a metal. We see, therefore, that, as regards its relations to light, the crystallized body passes repeatedly from the condition of a vitreous to that of a metallic substance and back again, as the refrangibility of the rays, in relation to which it is considered, is continuously increased by a small amount.

The same relation between intense absorption and metallic reflexion exists generally, though it cannot be always studied by means of a solution. The platinocyanides, for example, yield colourless solutions, so that the intense absorption which most of them exercise for certain parts of the spectrum must be attributed to the mode in which the molecules are built up in forming the crystals; but by attending to the colour of the light transmitted by thin crystals, the law is found to be obeyed. Gold can only be obtained, in solution, as gold by means of the opaque solvent mercury; but its colour by transmission may be studied in gold leaf, or in a chemically deposited film, and is then found to be conformable to be law mentioned, the less refrangible colours, which are those which are the more copiously reflected, being also those which are the more intensely absorbed.

When a body endowed with the property of coloured reflexion, such as permanganate of potash, is dissolved, in consequence of the necessary dilution, the opacity of the medium ceases to be, for any part of the spectrum, of that intense kind which is necessary for quasi-metallic reflexion; and accordingly the light reflected by the solution is colourless. Hence coloured reflexion is not available for following a substance through mixtures containing it. The chemist ought, however, to be acquainted with its laws, in order to understand the changes of colour which a substance possessing the property is capable of exhibiting in the solid condition, according to its state of aggregation.

In order that the colour due to reflexion should appear, it is necessary that the substance should have a certain amount of coherence. Thus indigo in the form of a fine loose powder is blue, even when viewed by reflexion. It would be erroneous, however, to describe the body as blue by reflexion, if we were speaking of the properties of the substance, and not the mere crude results of observation made under given circumstances. For though it is true that the light by which the blue colour is seen has undergone reflexion (without which it would not have reached the eye) it is not *in reflexion* that the chromatic selection is made by virtue of which the powder appears blue, but *during transmission*. In fact it is only a small portion of the light that is reflected at the outer irregular surface of the mass; the greater part penetrates a little way, and is reflected at various depths, and in passing through the particles, in going and returning, suffers absorption on the part of the coloured substance. Were the substance intensely opaque for *all* the colours of the spectrum, the powder would be not blue but black, as we see in the case of platinum-black. By burnishing, the powder is reduced to the state of a somewhat coherent mass, and it now begins to exhibit the copper colour due to reflexion. The internal reflexions are at the same time greatly weakened, so that the part of the light which is reflected from beneath and undergoes absorption is much reduced. A pressed mass is not, however, an optically homogeneous medium, so that the colour by reflexion obtained by burnishing cannot in general be quite pure. In the state of a fine crystalline powder, indigo exhibits a mixture of the copper colour due to reflexion, and the blue colour due to transmission, though observed in the light reflected from the mass as a whole; while if the substance could be obtained in large crystals, the colour by reflexion would be seen in perfection, and the colour by transmission would disappear, the crystals being sensibly opaque.

---

## XXXV.—*On the Properties of Silicic Acid and other Analogous Colloidal Substances.*

By Thomas Graham, F.R.S.

The prevalent notions respecting Solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal substances. Hydrated silicic acid, for instance, when in the soluble condition, is, properly speaking, a liquid body, like alcohol, miscible with water in all proportions. We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt, unless it be with reference to silicic acid in the gelatinous condition, in which it is usually looked upon as destitute of solubility. The jelly of silicic acid may be more or less rich in combined water, as it is first prepared, and it appears to be soluble in proportion to the extent of its hydration. A jelly containing 1 per cent. of silicic acid, gives with cold water a solution containing about 1 part of silicic acid in 5,000 water; a jelly containing 5 per cent. of silicic acid gives a solution containing about 1 part of acid in 10,000 water. A less hydrated jelly than the last mentioned is still less soluble; and, finally, when the jelly is rendered anhydrous, it forms gummy-looking white masses, which appear to be absolutely insoluble, like the light dusty silicic acid obtained by drying a jelly charged with salts, in the ordinary analysis of a silicate.

The liquidity of silicic acid is only affected by a change, which is permanent (namely, coagulation or pectization), by which the acid is converted into the gelatinous or pectous form, and loses its miscibility with water. This change may be brought about by time alone. The liquidity is permanent in proportion to the degree of dilution of silicic acid, and appears to be favoured by a low temperature. It is opposed, on the contrary, by concentration, and by elevation of temperature. A liquid silicic acid of 10 or 12 per cent. pectizes spontaneously in a few hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent. may be preserved for five or six days; a liquid of 2 per cent. for two or three months; and a liquid of 1 per cent. has not pectized after two years. Dilute solutions of 0·1 per cent. or less are no doubt practically unalterable by time, and hence the possibility of soluble silicic acid existing in nature. I may add, however, that no solution, weak or strong, of silicic acid in water has shown any disposition to deposit *crystals*, but always appears on drying as a colloidal glassy hyalite. The formation of quartz crystals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from solutions of silicic acid which are extremely dilute. Dilution no doubt weakens the colloidal character of substances, and may therefore allow their crystallizing tendency to gain ground and develope itself, particularly where the crystal once formed is completely insoluble, as with quartz.

The pectization of liquid sicilic acid is expedited by contact with solid matter in the form of powder. By contact with pounded graphite, which is chemically inactive, the pectization of a five per cent. silicic acid is brought about in an hour or two, and that of a 2 per cent. silicic acid in two days. A rise of temperature of 1°·1 C. was observed during the formation of the 5 per cent. jelly.

The ultimate pectization of sicilic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscocity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances, leads to pectization. In the jelly itself, the specific contraction in question, or *synæresis,* still proceeds, causing separation of water, with division into a clot and serum, and ending in the production of a hard stony mass of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense synæresis of isinglass dried in a glass dish over sulphuric acid *in vacuo,* enables the contracting gelatin to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatin, when dried in the manner described upon plates of calcspar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal synæresis.

Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but greatly more developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions. These characters appear in the viscidity of liquids, and in the softness and adhesiveness of certain crystalline substances. Metaphosphate of soda, after fusion by heat, is a true glass or colloid; but when this glass is maintained for a few minutes at a temperature some degrees under its point of fusion, the glass assumes a crystalline structure without losing its transparency. Notwithstanding this change, the low diffusibility of the salt is preserved, with other characters of a colloid. Water in the form of ice has already been represented as a similar intermediate form, both colloid and crystalline, and in the first character adhesive and capable of reunion or "regelation."

It is unnecessary to return here to the fact of the ready pectization of liquid silicic acid by alkaline salts, including some of very sparing solubility, such as carbonate of lime, beyond stating that the presence of carbonate of lime in water was observed to be incompatible with the co-existence of soluble silicic acid, till the proportion of the latter was reduced to nearly 1 in 10,000 water.

Certain liquid substances differ from the salts in exercising little or no pectizing influence upon liquid silicic acid. But, on the other hand, none of the liquids now referred to appear to conduce to the preservation of the fluidity of the colloid, at least not more than the addition of water would do. Among these inactive diluents of silicic acid are found hydrochloric, nitric, acetic, and tartaric acids, syrup of sugar, glycerin, and alcohol. But all the liquid substances named, and many others, appear to possess an important relation to silicic acid, of a very different nature from the pectizing action of salts. They are capable of displacing the combined water of the silicic acid hydrate, whether that hydrate is in the liquid or gelatinous condition, and give new substitution-products.

A liquid compound of *alcohol* and silicic acid is obtained by adding alcohol to aqueous silicic acid, and then employing proper means to withdraw the water from the mixture. For that purpose the mixture contained in a cup may be placed over dry carbonate of potash or quicklime, within the receiver of an air-pump. Or a dialyzing bag of parchment paper containing the mixed alcohol and silicic acid may be suspended in a jar of alcohol: the water diffuses away, leaving in the bag a liquid composed of alcohol and silicic acid only. A point to be attended to is, that the silicic acid should never be allowed to form more than 1 per cent. of the alcoholic solution, otherwise it may gelatinize during the experiment. If I may be allowed to distinguish the liquid and gelatinous hydrates of silicic acid by the irregularly formed terms of *hydrosol* and *hydrogel* of silicic acid, the two corresponding alcoholic bodies now introduced may be named the alcosol and alcogel of silicic acid.

The *alcosol* of silicic acid, containing 1 per cent. of the latter, is a colourless liquid, not precipitated by water or salts, nor by contact with insoluble powders, probably from the small proportion of silicic acid present in solution. It may be boiled and evaporated without change, but is gelatinized by a slight concentration. The alcohol is retained less strongly in the alcosol of silicic acid than water is in the hydrosol, but with the same varying force, a small portion of the alcohol being held so strongly as to char when the resulting jelly is rapidly distilled at a high temperature. Not a trace of silicic ether is found in any compound of this class. The jelly burns readily in the air, leaving the whole silicic acid in the form of a white ash.

The *alcogel*, or solid compound, is readily prepared by placing masses of gelatinous silicic acid, containing 8 or 10 per cent. of the dry acid in absolute alcohol, and changing the latter repeatedly till the water of the hydrogel is fully replaced by alcohol. The alcogel is generally slightly opalescent, and is similar in aspect to the hydrogel, preserving very nearly its original bulk. The following is the composition of an alcogel carefully prepared from a hydrogel which contained 9·35 per cent. of silicic acid:—

| | |
|---|---|
| Alcohol .............. | 88·13 |
| Water................. | 0·23 |
| Silicic acid............ | 11·64 |
| | 100·00 |

Placed in water, the alcogel is gradually decomposed—alcohol diffusing out and water entering instead, so that a hydrogel is reproduced.

Further the alcogel may be made the starting-point in the formation of a great variety of other substitution jellies of analogous constitution the only condition required appearing to be that the new liquid and alcohol should be intermiscible, that is, interdiffusible bodies. Compounds of ether, benzole, and bisulphide of carbon have thus been produced. Again, from *etherogel* another series of silicic acid jellies may be derived, containing fluids soluble in ether, such as the fixed oils.

The preparation of the *glycerin-compound* of silicic acid is facilitated by the comparative fixity of that liquid. When hydrated silicic acid is first steeped in glycerin, and then boiled in the same liquid, water distils over, without any change in the appearance of the jelly, except that when formerly opalescent it becomes now entirely colourless, and ceases to be visible when covered by the liquid. But a portion of the silicic acid is dissolved, and a *glycerosol* is produced at the same time as the glycerin jelly. A glycerogel prepared from a hydrate containing 9·35 per cent. of silicic acid, was found by a combustion analysis to be composed of—

| | |
|---|---|
| Glycerin | 87·44 |
| Water | 3·78 |
| Silicic acid | 8·95 |
| | 100·17 |

The glycerogel has somewhat less bulk than the original hydrogel. When a glycerine jelly is distilled by heat, it does not fuse, but the whole of the glycerine comes over, with a slight amount of decomposition towards the end of the process.

The compound of sulphuric acid, *sulphagel*, is also interesting from the facility of its formation, and the complete manner in which the water of the original hydrogel is removed. A mass of hydrated silicic acid may be preserved unbroken if it is first placed in sulphuric acid diluted with two or three volumes of water, and then transferred gradually to stronger acids, till at last it is placed in concentrated oil of vitriol. The sulphagel sinks in the latter fluid. and may be distilled with an excess of it for hours without losing its transparency or gelatinous character. It is always somewhat less in bulk than the primary hydrogel, but not more, to the eye, than one-fifth or one-sixth part of the original volume. This sulphagel is transparent and colourless. When a sulphagel is heated strongly in an open vessel, the last portions of the monohydrated sulphuric acid in combination are found to require a higher temperature for their expulsion, than the boiling-point of the acid. The whole silicic acid remains behind, forming a white opaque, porous mass, like pumice. A sulphagel placed in water is soon decomposed, and the original hydrogel reproduced. No permanent compound of sulphuric and silicic acids, of the nature of a salt, appears to be formed in any circumstances. A sulphagel placed in alcohol gives ultimately a pure alcogel. Similar jellies of silicic acid may readily be formed with the monohydrates of nitric, acetic, and formic acids, and are all perfectly transparent.

The production of the compounds of silicic acid now described, indicates the possession of a wider range of affinity by a colloid than could well be anticipated. The organic colloids are no doubt invested with similar wide powers of combination, which may become of interest to the physiologist. The capacity of a mass of gelatinous silicic acid to assume alcohol, or even olein, in the place of water of combination, without disintegration or alteration of form, may perhaps afford a clue to the penetration of the albuminous matter of membrane by fatty and other insoluble bodies, which seems to occur in the digestion of food. Still more remarkable and suggestive are the *fluid* compounds of silicic acid. The fluid alcohol-compound favours the possibility of the existence of a compound of the colloid albumin with olein, soluble also and capable of circulating with the blood.

The feebleness of the force which holds together two substances belonging to different physical classes, one being a colloid and the other a crystalloid, is a subject deserving notice. When such a compound is placed in a fluid, the superior diffusive energy of the crystalloid may cause its separation from the colloid. Thus, of hydrated silicic acid, the combined water (a crystalloid) leaves the acid (a colloid) to diffuse into alcohol; and if the alcohol be repeatedly changed, the entire water, is thus removed, alcohol (another crystalloid) at the same time taking the place of water in combination with the silicic acid. The liquid in excess (here the alcohol) gains entire possession of the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Then alcohol separates from combination, in consequence of the opportunity it possesses to diffuse into water; and water, which is now the liquid present in excess, recovers possession of the silicic acid. Such changes illustrate the predominating influence of mass.

Even the compounds of silicic acid with alkalies, yield to the decomposing force of diffusion. The compound of silicic acid with 1 or 2 per cent. of soda is a colloidal solution, and, when placed in a dialyser over water *in vacuo* to exclude carbonic acid, suffers gradual decomposition. The soda diffuses off slowly in the caustic state, and gives the usual brown oxide of silver when tested with the nitrate of that base.

The pectization of liquid silicic acid and many other liquid colloids, is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may again be liquefied and have its energy restored by contact with a very moderate amount of alkali. The latter change is gradual, 1 part of caustic soda, dissolved 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100° C. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyser. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid, but alkaline. Liquid silicic acid may be represented as the "peptone" of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali, may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron, and titanic acid, prepared by dialysis, are assimilated more closely to albumin, being peptized by minute quantities of hydrochloric acid.

*Liquid Stannic and Metastannic Acids.*—Liquid stannic acid is prepared by dialysing the bichloride of tin with an addition of alkali, or by dialysing the stannate of soda with an addition of hydrochloric acid. In both cases a jelly is first formed on the dialyser; but, as the salts diffuse away, the jelly is again peptized by the small proportion of free alkali remaining: the alkali itself may be removed by continued diffusion, a drop or two of the tincture of iodine facilitating the separation. The liquid stannic acid is converted, on heating it, into liquid metastannic acid. Both liquid acids are remarkable for the facility with which they are pectized by a minute addition of hydrochloric acid, as well as by salts.

*Liquid Titanic Acid* is prepared by dissolving gelatinous titanic acid in a small quantity of hydrochloric acid, without heat, and placing the liquid upon a dialyser for several days. The liquid must not contain more than 1 per cent. of titanic acid, otherwise it gelatinizes spontaneously, but it appears more stable when dilute. Both titanic and the two stannic acids afford the same classes of compounds with alcohols, &c., as are obtained with silicic acid.

*Liquid Tungstic Acid.*—The obscurity which has so long hung over tungstic acid is removed by a dialytic examination. It is in fact a remarkable colloid, of which the pectous form alone has hitherto been known. Liquid tungstic acid is prepared by adding dilute hydrochloric acid carefully, and in slight excess to a 5 per cent. solution of tungstate of soda, and then placing the resulting liquid on a dialyser. At intervals of two days, the addition of hydrochloric acid must be repeated two or three times, and the dialysis continued in order to remove the whole alkali. It is remarkable that the *purified* acid is not pectized by acids, salts, or alcohol at the ordinary temperature. Evaporated to dryness, it forms vitreous scales, like gum or gelatin, which sometimes adhere so strongly to the surface of the evaporating dish as to detach portions of it. It may be heated to 200° C. without losing its solubility, or passing into the pectous state, but, at a temperature near redness, it undergoes a molecular change, closing at the same time 2·42 per cent. of water. When water is added to unchanged tungstic acid, the acid becomes pasty and adhesive, like gum ; and it forms a liquid with about one-fourth its weight in water, which is so dense as to float glass. The solution effervesces with carbonate of soda. The taste of tungstic acid dissolved in water is not metallic or acid, but rather bitter and astringent. Solutions of tungstic acid containing 5, 20, 50, 66·5, and 79·8 per cent. of dry acid, possess the following densities at 19°: 1·0475, 1·2168, 1·8001, 2·396, and 3·243. Evaporated *in vacuo*, liquid tungstic acid is colourless, but becomes greenish in air, apparently from the deoxidating action of organic matter. Liquid silicic acid is protected from pectizing when mixed with tungstic acid, a circumstance probably connected with the formation of the double compounds of these two acids which M. Marignac has lately indicated.

*Molybdic Acid* has hitherto been known (like tungstic acid) only in the insoluble form. Crystallized molybdate of soda dissolved in water is decomposed by the gradual addition of hydrochloric acid in excess, without any immediate precipitation. The acid liquid thrown upon a dialyser may gelatinize after a few hours, but again liquefies spontaneously, when the salts diffuse away. After repeated additions of hydrochloric acid, and a diffusion of several days, about 60 per cent. of liquid molybdic acid remains behind in a pure condition. In the dialysis of both tungstic and molybdic acids, the osmose is very great, the acid solutions increasing to two or three times their original volume. The consequent dilution causes the purification to be slow, as compared with that of silicic acid where the osmose is inconsiderable. The solution of pure molybdic acid is yellow, astringent to the taste, acid to test-paper, and possesses much stability. The acid may be dried at 100°, without immediately losing its solubility. Dry molybdic acid has the same gummy aspect as tungstic acid. Heated short of the point at which it volatilizes, pure molybdic acid in powder will still dissolve in a solution of carbonate or bicarbonate of potash, with effervescence of carbonic acid gas. Both acids lose their colloidality when combined with soda, and give a variety of crystallizable salts. The pure liquid acids also become insoluble, when heated for some time with hydrochloric or other strong acids.

# XXXVI.—*Action of Chloride of Iodine on certain Organic Substances.*

By JOHN STENHOUSE, LL.D., F.R.S., &c.

So far as I am aware, chloride of iodine was first employed to act on organic substances by Mr. J. F. Brown in 1851,* who produced, by means of this reagent, iodo-pyromeconic acid and iodomecone. The chloride of iodine which was employed in the subjoined experiments was prepared by passing chlorine into a retort containing moist iodine, care being taken to keep the iodine in excess. The product was then agitated with a considerable quantity of water, and allowed to stand some time to enable the excess of iodine to subside. The clear brownish-yellow solution of chloride of iodine thus obtained was the reagent employed.

## *Action of Chloride of Iodine on Orcin.*

TERIODORCIN.—On adding chloride of iodine to a dilute aqueous solution of orcin, a yellowish-brown precipitate is produced, which quickly collects at the bottom of the vessel as a soft adhesive mass, which, however, on standing some time, becomes hard and brittle. Care should be taken to leave the orcin slightly in excess, by adding the chloride of iodine in quantity insufficient to precipitate the whole of it. The brownish-yellow mass thus obtained should be collected, washed with water, and dried. The dried precipitate is then dissolved in a considerable quantity of boiling bisulphide of carbon, and filtered. This separates it from a dark brown, resinous-looking substance, which remains undissolved. The greater portion of the bisulphide of carbon should then be got rid of by distillation. This is necessary, owing to the ready solubility of teriodorcin in that menstruum. The crystals obtained on the cooling of the solution are drained from the dark brown mother-liquors, and washed with a small quantity of cold bisulphide. Having been pressed between folds of bibulous paper, they are twice recrystallised from boiling spirit of wine. The teriodorcin, as obtained by this process, crystallises in large, transparent, brittle plates, tinged with brown, somewhat resembling chloride of barium in appearance. These crystals are very soluble in bisulphide of carbon, still more so in ether, and moderately soluble in alcohol, but insoluble in water.

---

* Phil. Mag. [4], viii, 201.

When heated to 100° they gradually become brown. They dissolve in caustic alkalis, decomposing, however, and yielding deep brown solutions. Strong nitric acid slowly decomposes them, even in the cold, and rapidly on heating, when nitrous fumes and the characteristic violet vapour of iodine are evolved. Sulphuric acid has no action in the cold, but on the application of heat the crystals char and give off vapour of iodine.

The crystals dried *in vacuo* over sulphuric acid were submitted to analysis, with the following results:—

I. ·365 grm. substance gave ·5115 grm. AgI.
II. ·466 grm. ,, ,, ·654 grm. ,,
III. ·613 grm. ,, ,, ·370 grm. carbonic acid, and ·065 grm. water.

| | | | | I. | II. | II. |
|---|---|---|---|---|---|---|
| $C_{14}$ | = | 84 | 16·73 | — | — | 16·46 |
| $H_5$ | = | 5 | 1·00 | — | — | 1·17 |
| $I_3$ | = | 381 | 75·90 | 75·71 | 75·84 | — |
| $O_4$ | = | 32 | 6·37 | | | |
| | | 502 | 100·00 | | | |

There can be no doubt, therefore, that the substance produced by the action of chloride of iodine on orcin, is orcin $C_{14}H_8O_4$, having 3 equivalents of hydrogen replaced by iodine $=C_{14}H_5I_3O_4$, being thus perfectly analogous to the bromine-substitution-compound.

### *Action of Chloride of Iodine on Aniline.*

When an aqueous solution of chloride of iodine containing a slight excess of iodine is added in considerable quantity to an aqueous solution of any of the salts of aniline, a copious dirty bluish-black amorphous precipitate is produced. When this precipitate is boiled with a large quantity of very dilute hydrochloric acid and filtered, the clear liquid, on being treated with an excess of ammonia, yields a small quantity of a white crystalline precipitate. This precipitate, which is tolerably soluble in hot spirit, separates on cooling in long brilliant needles, having a slight red tinge. These crystals cannot, however, be advantageously prepared by this method, but the following process yields them readily:—Very pure nitrate of aniline is prepared by dissolving aniline boiling between 180° and 185° C. in dilute nitric acid, and subsequently crystallising several times from water and alcohol. This salt is dissolved in a large quantity of cold water, and a small quantity of a moderately strong solution of chloride of iodine is added. A bluish-green precipitate is produced, which speedily becomes almost black, closely resembling that obtained by the former process, and consisting almost entirely of amorphous substance, with a few crystals. This black precipitate is separated by filtration, and the clear pink filtrate is then again treated in a similar manner. The second precipitate is less dark-coloured than the first. After three or four partial precipitations with chloride of iodine, the product is no longer black, but of a dirty greenish tint, and distinctly crystalline. These crystals are a mixture of needles and scales. Small quantities of chloride of iodine are now successively added to the filtrate, the precipitate being collected after each addition; care must be taken, however, not to add an excess of the chloride, as this is liable to alter the nature of the product; for this reason it is advisable that the last portion which is precipitated should be rejected, or at any rate kept separate from the preceding portions. The slightly coloured and highly crystalline portions obtained after the first two or three precipitations, and previous to the last, were those which I employed in this examination.. This crystalline precipitate, after being thoroughly dried at a gentle heat, is repeatedly boiled with bisulphide of carbon, which dissolves the needles, and leaves the scales, which are quite insoluble in that menstruum. The excess of the solvent is removed by distillation, and after standing for some time, the solution solidifies into a crystalline magma. This dark-coloured mass is thrown on a filter, drained from the mother-liquor, and then washed with a small quantity of cold bisulphide, by which means much of the dark-coloured substance is removed. On subsequently dissolving the partially purified crystals in boiling bisulphide of carbon, filtering from a small quantity of dark-coloured matter, which remains undissolved, and distilling off the excess of the solvent. The solution deposits crystals on cooling. These are freed from the impure mother-liquor by throwing them on a filter and washing them as before. A large quantity of the substance may likewise be obtained from the various mother-liquors by removing the bisulphide of carbon, and proceeding to purify the product in the manner already described. In order to render the nearly white crystals obtained by this process quite pure, they must first be boiled with a small quantity of spirit, which frees them from an adhering trace of yellowish brown substance. They are then crystallised two or three times from a large quantity of boiling spirit. As thus obtained, they consist of brilliant needles, sometimes several inches in length, and bearing a considerable resemblance to sublimed phthalic acid. The substance is insoluble in hot and cold water, slightly soluble in dilute hydrochloric acid, from which it is precipitated by ammonia; very soluble in bisulphide of carbon; sparingly soluble in ether, from which it crystallises on evaporation; but the most convenient solvent is alcohol, in which it is moderately soluble.

Strong nitric acid decomposes the crystals, even in the cold, and on heating they dissolve, and fumes of iodine are evolved. Concentrated sulphuric acid has no action on them in the cold, but on gently heating they are dissolved, and precipitated unchanged on the addition of water; if, however, the temperature be raised nearly to the boiling point of the sulphuric acid, the solution becomes purple, and violet vapours of iodine are given off. Ammonia and strong solutions of the caustic alkalis have no action on the substance, even at 100°.

The crystals, after being dried in vacuo over sulphuric acid, did not lose weight at 100°; they were therefore submitted to analysis.

I.— ·653 grm. substance gave ·798 grm. AgI.
II.— ·659 „ „ ·805 „
III.—1·346 „ „ ·7765 grm. carbonic acid, and ·126 grm. water.
IV.—1·372 grm. substance gave ·7830 grm. carbonic acid, and ·136 grm. water.
V.— ·849 grm. substance gave ·02827 grm. nitrogen.
VI.—1·117 grm. substance gave ·2445 grm. platinum.

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| C | — | — | 15·74 | 15·57 | — | — |
| H | — | — | 1·04 | 1·10 | — | — |
| I | 66·44 | 66·01 | — | — | — | — |
| N | — | — | — | — | 3·33 | 3·1 |

The substance employed in the above analyses was prepared at different times, and though perfectly homogeneous and in fine crystals, it was found to contain nearly half a per cent. of chlorine, which I regard as an accidental impurity. I have not been able to deduce a satisfactory formula, or to determine the atomic weight of this substance, as I have not succeeded in producing any of its combinations. It is clearly not a simple aniline substitution-compound, but probably belongs to some new class of combinations.

Oxalate of aniline when treated in a similar manner, yields the same products as the nitrate, although the latter is the best source, as the crystals obtained from it are much more easily purified. I should expect that the other soluble salts of aniline would yield the same product when treated with chloride of iodine. The compound already referred to as consisting of scales, which remains undissolved on treating the crude substance with boiling bisulphide of carbon in the preparation of the needles, occurs in comparatively small quantity, and has a purplish hue. On attempting to purify these scales by crystallising them from hot spirit, they decomposed so rapidly that, after the filtration of the boiling solution, only a small quantity crystallised out; these were now of a much paler colour, and rather grey than purple. Their most characteristic property is, that when strongly heated they fuse and then explode, giving off vapours of iodine. Owing to the very small amount of scales that can be procured by the above method, and the difficulties hitherto experienced in their purification, I have not succeeded in ascertaining their composition.

The dark-coloured amorphous substance, previously described as being obtained on the first precipitation of the salts of aniline by chloride of iodine, partly dissolves in *cold* alcohol, yielding a deep green solution, which becomes purple on the application of heat. It also dissolves in concentrated sulphuric acid with a purple colour, and is precipitated on the addition of water.

### *Action of the Chloride of Iodine on Salicin and Phloridzin.*

If a rather strong aqueous solution of salicin be treated with chloride of iodine, and allowed to stand for some time, it solidifies to a crystalline magma of white needles. These contain iodine, but I have not yet examined them further; I could not succeed in obtaining any definite crystalline compound from phloridzin by acting on it with chloride of iodine, the products being amorphous.

### *Action of Chloride of Iodine on Carbazotic Acid.*

When carbazotic acid is dissolved in a strong solution of chloride of iodine, and digested for some hours, the solution becomes of a deep brown colour ; if this be now submitted to distillation, vapour of iodine begins to arise, and a yellowish brown liquid passes over, smelling strongly of chloropicrin. After a considerable quantity of liquid has distilled, so that the solution in the retort is very concentrated, a large quantity of iodine volatilises, and is deposited in the neck. The distillation should now be stopped, the residue in the retort mixed with water, and the yellow scales which float in the liquid collected on a filter ; these, after being well washed with boiling water, and recrystallised from alcohol, present all the characteristic physical properties and chemical reactions of chloranil. The absence of iodine from both compounds was ascertained. It appears, therefore, that by the action of chloride of iodine on carbazotic acid, only chlorinated products are obtained. the chief of which are chloropicrin, and chloranil, the iodine being separated in the free state.

### *Action of Chloride of Iodine on Benzoic Acid.*

If an aqueous solution of benzoic acid be mixed with chloride of iodine solution, the former being in excess and allowed to stand for some time, the mixture gradually acquires a brown colour, and after twenty-four hours, a number of black and white crystals are deposited, the black ones being simply iodine, and the white a mixture of the chlorinated benzoic acids.

From the results of the preceeding experiments, it appears that the action of chloride of iodine on organic substances, is very variable. Sometimes the chlorine in the chloride of iodine acts merely as an introducer of the iodine into the compound; at others, the chlorine acts as when uncombined, the iodine of the chloride of iodine being separated in the free state, and remaining quite inactive.

The analyses in this paper were performed for me by my assistant, Mr. Charles Edward Groves.

## XXXVII.—*Note on Morindone.*

### By JOHN STENHOUSE, LL.D., F.R.S., &c.

IN 1819[*] Professor Thomas Anderson examined the root of the *Morinda citrafolia*, the "Al" root of the Hindoos, which is extensively used as a dye-stuff, chiefly in the Madras Presidency, and obtained from it a pale yellow crystalline body, to which he gave the name of *Morindin.* When morindin was subjected to distillation, it yielded a reddish yellow crystalline sublimate, to which he gave the name of *Morindone.* Anderson likewise found that morindin was incapable of dying cloth mordanted in the usual way, but that, with the Turkey red mordant, it produced permanent, but very dull red colours: while morindone was a true dye-stuff, and yielded the bright colours of ordinary madder.

In 1852,[†] Professor Rochleder, from the consideration of Anderson's statements, gave it as his opinion, that morindin was identical with the ruberythric acid which he himself had obtained from madder, and that morindone was alizarin. About eighteen months ago I was fortunate enough to obtain a very small quantity of "Al" root, from which I extracted the morindin by Anderson's process. When cautiously heated in a Mohr's apparatus, it was decomposed, yielding a sublimate of bright yellowish red needles, which had all the physical and chemical properties of alizarin. I transmitted a small quantity of the substance to Professor Stokes, who, after examination, informs me that it has the spectrum of alizarin, as may be seen by the following extract from a letter I received from him, April 2nd, 1863:—

"*Anderson's Morindone.*—The ethereal solution, like that of alizarin, causes a general absorption of the highly refrangible rays without the distinctive bands of purpurin. The solution in carbonate of soda shows the peculiar system of absorption-bands of a similar solution of alizarin, and moreover shows the same reaction with a solution of alum and tartaric acid, rendered slightly alkaline. This removes the three alizarin-bands and establishes a broad minimum a little further on in the spectrum." There can be no doubt therefore that Anderson's morindone, of which he made only one analysis, is simply alizarin. Whether Rochleder's second conjecture is correct, that ruberythric acid and morindin are the same substance, I am unable to determine.

---

[*] Trans Royal Soc Edin, xvi., 435.

[†] Ann. Ch. Pharm., lxxvii, 205.

When powdered morinda-root is boiled with moderately dilute sulphuric acid, as in the ordinary garancin process, its morindin is converted into alizarin; but the large quantity of brown resinous matter which is produced at the same time, very greatly diminishes the value of the dye-stuff obtained, as it renders the colours dull and the whites very difficult to clear. Though "Al" root therefore is never likely, at least in Europe, to compete successfully with madder, still it furnishes the scientific chemist with the best known source of *pure* alizarin; for, as is well known, it is by no means easy to separate the last trace of purpurin, which always accompanies alizarin in ordinary madder.

---

## XXXVIII.—*On the Molecular Mobility of Gases.*

By Thomas Graham, F.R.S., Master of the Mint.

(From the Philosophical Transactions for 1863.)

The molecular mobility of gases will be considered at present chiefly with reference to the passage of gases, under pressure, through a thin porous plate or septum, and to the partial separation of mixed gases, which can be effected, as will be shown, by such means. The investigation arose out of a renewed and somewhat protracted inquiry regarding the diffusion of gases (which depends upon the same molecular mobility), and has afforded certain new results which may prove to be of interest in a theoretical as well as in a practical point of view.

In the Diffusiometer, as first constructed, a plain cylindrical glass tube, about 10 inches in length and rather less than an inch in diameter, was simply closed at one end by a porous plate of plaster of Paris, about one-third of an inch in thickness, and was thus converted into a gas-receiver*. A superior material for the porous plate has since been found in the artificially compressed

---

* "On the Law of the Diffusion of Gases," Transactions of the Royal Society of Edinburgh, vol. xii, p. 222; or Philosophical Magazine, 1834, vol. ii, pp. 175, 269, 351.

Fig 1.

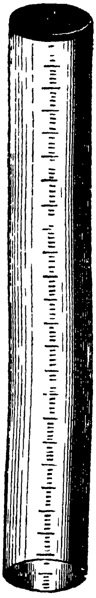
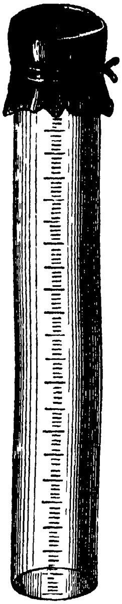


Fig. 2.



graphite of Mr. Brockedon, of the quality used for making writing-pencils. This material is sold in London in small cubic masses about 2 inches square. A cube may easily be cut into slices of a millimetre or two in thickness by means of a saw of steel spring. By rubbing the surface of the slice, without wetting it, upon a flat sand-stone, the thickness may be further reduced to about one-half of a millimetre. A circular disc of this graphite, which is like a wafer in thickness, but possesses considerable tenacity, is attached by resinous cement to one end of the glass tube above described, so as to close it and form a diffusiometer (Fig. 1). The tube is filled with hydrogen gas over a mercurial trough, the porosity of the graphite plate being counteracted for the time by covering it tightly with a thin sheet of gutta-percha (Fig. 2). On afterwards removing the latter, gaseous diffusion immediately takes place through the pores of the graphite. The whole hydrogen leaves the tube in forty minutes or an hour, and is replaced by a much smaller proportion of atmospheric air (about one-fourth), as is to be expected from the law of the diffusion of gases. During the process, the mercury will rise in the tube, if allowed, forming a column of several inches in height—a fact which illustrates strikingly the intensity of the force with which the interpenetration of different gases is effected. Native graphite is of a lamellar structure, and appears to have little or no porosity. It cannot be substituted for the artificial graphite as a diffusion-septum. Unglazed earthenware comes next in value to graphite for that purpose.

The pores of artificial graphite appear to be really so minute, that a gas *in mass* cannot penetrate the plate at all. It seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores that can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement of molecules which is now generally recognised as an essential property of the gaseous condition of matter.

According to the physical hypothesis now generally received*, a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel, the moving particles are constantly impinging against its sides and occasionally against each other, and this contact takes place without any loss of motion, owing to the perfect elasticity of the particles. If the containing vessel be porous, like a diffusiometer, then gas is projected through the open channels, by the atomic motion described, and escapes. Simultaneously the external air is carried inwards in the same manner, and takes the place of the gas which leaves the vessel. To this atomic or molecular movement is due the elastic force, with the power to resist compression, possessed by gases. The molecular movement is accelerated by heat and retarded by cold, the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, or is in contact with both sides of our porous plate, the movement is sustained without abatement—molecules continuing to enter and leave the vessel in equal number, although nothing of the kind is indicated by change of volume or otherwise. If the gases in communication be different, but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the permeation ceases of course to be equal in both directions.

These observations are preliminary to the consideration of the passage through a graphite plate, in one direction only, of gas under pressure, or under the influence of its own elastic force. We are to suppose a vacuum to be maintained on one side of the porous septum, and air or any other gas, under a constant pressure, to be in contact with the other side. Now a gas may pass into a vacuum in three different modes, or in two other modes besides that immediately before us.

---

* D. Bernoulli, J. Herapath, Joule, Krönig, Clausius, Clerk Maxwell and Cazin. The merit of reviving this hypothesis in recent times and first applying it to the facts of gaseous diffusion, is fairly due to Mr. Herapath. See "Mathematical Physics," in two volumes, by John Herapath, Esq (1847).

1. The gas may enter the vacuum by passing through a minute aperture in a thin plate, such as a puncture in platinum foil made by a fine steel point. The rate of passage of different gases is then regulated by their specific gravities, according to a pneumatic law which was deduced by Professor John Robison from Torricelli's well-known theorem of the velocity of efflux of fluids. A gas rushes into a vacuum with the velocity which a heavy body would acquire by falling from the height of an atmosphere composed of the gas in question, and supposed to be of uniform density throughout. The height of the uniform atmosphere would be inversely as the density of the gas, the atmosphere of hydrogen, for instance, 16 times higher than that of oxygen. But as the velocity acquired by a heavy body in falling is not directly as the height, but as the square root of the height, the rate of flow of different gases into a vacuum will be inversely as the square root of their respective densities. The velocity of oxygen being 1, that of hydrogen will be 4, the square root of 16. This law has been experimentally verified.* The relative times of the effusion of gases, as I have spoken of it, are similar to those of molecular diffusion; but it is important to observe that the phenomena of effusion and diffusion are distinct and essentially different in their nature. The effusion movement affects masses of gas, the diffusion movement affects molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times as great as is demonstrable by the latter.

2. If the aperture of efflux be in a plate of increased thickness, and so becomes a tube, the effusion-rates are disturbed. The rates of flow of different gases, however, assume again a constant ratio to each other when the capillary tube is considerably elongated, when the length exceeds the diameter by at least 4,000 times. These new proportions of efflux are the rates of the "Capillary Transpiration" of gases.† The rates are found to be the same in a capillary tube composed of copper, as they are in glass, and appear to be independent of the material of the capillary. A film of gas, no doubt, adheres to the surface of the tube, and the friction is really that of gas upon gas, and is consequently unaffected by the tube-substance. The rates of transpiration are not governed by specific gravity, and are indeed singularly unlike the rates of effusion.

---

* "On the Motion of Gases," Philosophical Transactions, 1846, p. 573.

† Ibidem p. 591; and Philosophical Transactions, 1849, p. 349.

The transpiration-velocity of oxygen being 1, that of chlorine is 1·5, that of hydrogen 2·26, of ether-vapour the same or nearly the same as that of hydrogen, of nitrogen and carbonic oxide half that of hydrogen, of olefiant gas, ammonia, and cyanogen, 2 (double, or nearly double that of oxygen), of carbonic acid 1·376, and of the gas of marshes, 1·815. In the same gas, the velocity of transpiration increases with increased density, whether occasioned by cold or pressure.

The transpiration-ratios of gases appear to be in direct relation with no other known property of the same gases, and they form a class of phenomena remarkably isolated from all else at present known of gases.

There is one property of transpiration immediately bearing upon permeation of the graphite plate by gases. The capillary offers to the passage of gas a resistance analogous to that of friction, proportional to the surface, and consequently increasing as the tube or tubes are multiplied in number and diminished in diameter, with the area of discharge preserved constant. The resistance to the passage of liquid through a capillary was observed by Poiseuille to be nearly as the fourth power of the diameter of the tube. In gases the resistance also rapidly increases; but in what ratio, has not been observed. The consequence, however, is certain, that, as the diameter of the capillaries may be diminished beyond any assignable limit, so the flow may be retarded indefinitely, and caused at last to become too small to be sensible. We may then have a mass of capillaries, of which the passages form a large aggregate, but are individually too small to allow a sensible flow of gas under pressure. A porous solid mass may possess the same reduced permeability as the congeries of capillary tubes. Indeed the state of porosity described appears to be more or less closely approached by all loosely aggregated mineral masses, such as lime-plaster, stucco, chalk, baked clay, non-crystalline earthy powders, like hydrate of lime or magnesia compacted by pressure, and in the highest degree, perhaps, by artificial graphite.

3. A plate of artificial graphite, although it appears to be practically impermeable to gas by either of the two modes of passage previously described, is readily penetrated by the agency of the molecular or diffusive movement of gases. This appears on comparing the time required for the passage through the plate of equal volumes of different gases under a constant pressure. Of the three gases, oxygen, hydrogen, and carbonic acid, the time

required for the passage of an equal volume of each through a capillary glass tube, in similar circumstances as to pressure and temperature, was formerly observed to be as follows:—

| | Time of capillary transpiration of equal volumes. |
|---|---|
| Oxygen | 1 |
| Hydrogen | 0·44 |
| Carbonic acid | 0·72 |

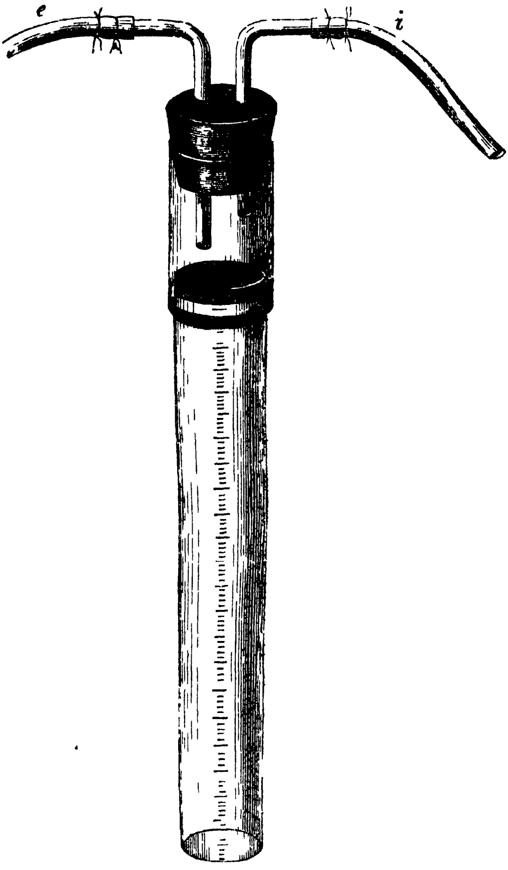
Now through a plate of graphite, half a millimetre in thickness, the same gases were observed to pass, under a constant pressure of a column of mercury of 100 millimetres in height, in times which are as follows:—

| | Time of molecular passage. | Square root of density (oxygen 1). |
|---|---|---|
| Oxygen | 1 | 1 |
| Hydrogen | 0·2472 | 0·2502 |
| Carbonic acid | 1·1886 | 1·1760 |

It appears that the times of passage through the graphite plate have no relation to the capillary transpiration-times of the same gases as first quoted. The new times in question, however, show a close relation to the square roots of the densities of the respective gases, as is seen in the last table; and they so far agree with the theoretical *times of diffusion* usually ascribed to the same gases.

These results were obtained by means of the graphite diffusiometer already referred to, which was a plain glass tube about 22 millimetres in diameter, closed at one end by the graphite plate. In order to conduct gas to the upper surface of the graphite plate, a little chamber was formed above the plate, to which the gas was conveyed in a moderate stream by the entrance-tube *e* (Fig. 3), while the gas brought in excess was constantly escaping into the air by the open issue-tube *i*. The chamber was formed of a short piece of glass tube, about 2 inches in length, cemented over the upper end of the diffusiometer. The upper opening of this short tube was closed by a cork perforated for the entrance- and exit tubes. It will be observed that by this arrangement the upper surface of the graphite plate was constantly swept by a stream of gas, which was under no additional pressure beyond that of the atmosphere, a free escape being allowed by the exit-tube. The

Fig. 3.



gas also was always dried before reaching the chamber. The diffusiometer stood over mercury, and was raised or lowered by the lever movement introduced by Professor Bunsen in his very exact experiments upon gaseous diffusion*. To obtain the pressure of 100 millimetres of mercury, the diffusiometer was first entirely filled with mercury and then raised in the trough. Gas gradually entered till the column of mercury in the tube fell to 100 millimetres. The mercury was then maintained at this height, by gradually raising the tube in proportion as gas continued to enter and the mercury to fall, so as to maintain a constant difference of level of 100 millimetres, as observed by the graduation inscribed upon the tube itself, between the level of the mercury in the tube and trough. The experiment consisted in observing the time in seconds which the mercury took to fall 10 millimetre divisions with each gas. The constant volume of gas which entered was 2·2 cubic centimetres (0·1342 cubic inch). Two experiments were made with each gas.

Oxygen entered in 898 and 894 seconds; mean 896 seconds.
Hydrogen in 222 and 221 seconds; mean 221·5 seconds.
Carbonic acid in 1070 and 1060 seconds; mean 1065 seconds.

---

* Bunsen's "Gasometry," translated by Roscoe.

In such experiments the same gas exists on both sides, and also occupies the pores of the diaphragm. But the molecular movement within the pores in a downward direction is not fully balanced by the molecular movement in an upward direction, owing to the less tension, by 100 millimetres, of the gas below the diaphragm and within the tube than the gas above and without. The influx of gas indicates the difference of molecular movement in opposite directions. Taking the full tension of the gas above the diaphragm at 760 millimetres, that below would be 660 millimetres, and the movement downwards and that upwards are represented by these numbers respectively.

To increase the inequality of tension and favour the passage of gas through the graphite plate, a diffusion-tube was now used, 48 inches in length, or of the dimensions of a barometer-tube, by which a Torricellian vacuum could be commanded. The pneumatic trough in which this gas-tube was suspended consisted of a pipe of gutta-percha of equal length, closed at the bottom by a cork, and widening into a funnel-form at the top. In one modification of the instrument, it was found convenient to cement a capillary glass tube to the side of the glass diffusiometer, within about 15 millimetres of the upper end of the tube. An opening into the upper part of the glass tube was thus obtained, by means of which the gas contained in the diffusiometer could escape when the latter was depressed in the mercurial trough. A flexible tube with clip was attached to the capillary tube referred to, so that the latter could be closed From the same opening a specimen of the gas contained in the diffusiometer could be drawn when required for examination.

In another and more serviceable modification of this barometrical diffusiometer, a large space was obtained above the mercurial column, by surmounting the long glass tube, unprovided with a graphite plate, by a glass jar about half a litre in capacity. This jar was more correctly a small bell jar (Fig. 4) open at top. It was fitted in an inverted position, as in Fig. 5, to the open end of the long glass tube *d*, by means of a cork and cement. The large upper opening was closed by a circular plate of gutta-percha (Fig. 5), about 10 millimetres, or nearly half an inch, in thickness. This disc of gutta-percha had two perforations at *f* and *g* (Fig. 6), the former of which was fitted above with a wide glass tube. The tube *f* was closed below by the plate of graphite, and above with a perforated cork carrying a quill tube, *e*. This quill tube was the entrance-tube for gas, and was accompanied by the usual issue-tube, *i*. The other aperture in the gutta-percha cover was

Fig. 4.

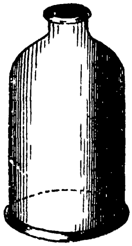


Fig. 5.

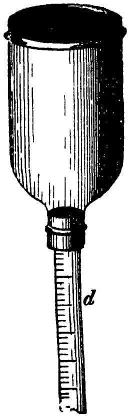
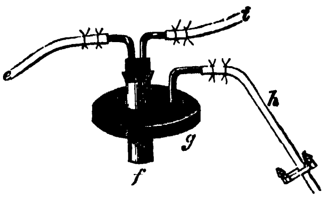


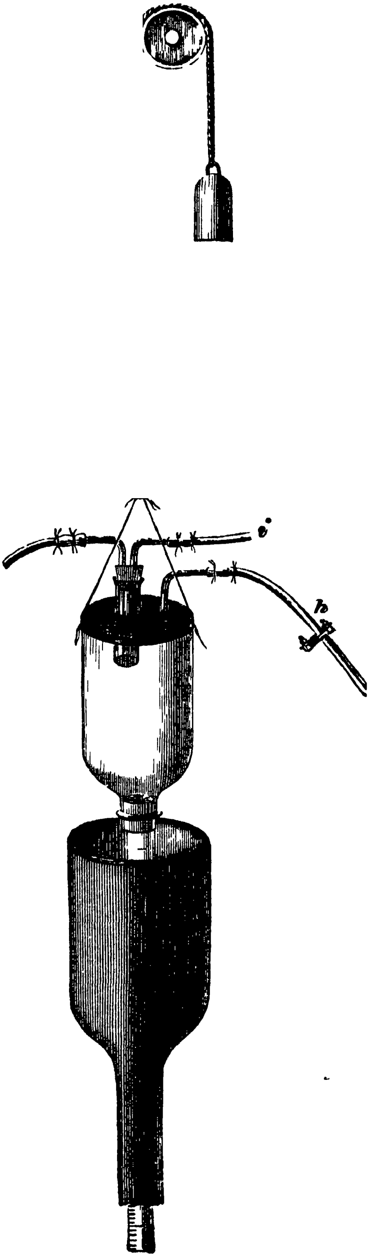
Fig. 6.



fitted with a plain quill-tube *h*, which did not descend below the level of the gutta-percha, and formed a tube of exit. No difficulty was found in making all these junctions air-tight, by applying the heated blade of a knife to fuse the gutta-percha in contact with the glass. Gutta-percha is, indeed, of no ordinary value in the construction of pneumatic apparatus. The graphite plate itself required to be not less than 1 millimetre in thickness, in order to support the pressure of a whole atmosphere, to which it is exposed in the present apparatus. This barometrical diffusiometer is supported from above by a chord passing over a pulley, and is duly counterpoised by a hanging weight.

In operating, the first point is to expel the air from the barometer tube and upper chamber. The instrument (Fig. 7) is sunk completely in the mercurial trough previously described, till the whole is filled, and mercury enters the quill tube of exit, *h*. The caoutchouc extension of this tube is then closed by a pinch. The diffusiometer is now elevated 30 or 40 inches, when the mercury sinks in the glass tube till it comes to stand at the barometric height for the time, leaving the upper chamber entirely vacuous. The gas to be tried has in the mean time been made to stream over the upper surface of the graphite plate, exactly as in the experiment with the former diffusiometer. The graphite is per-

Fig. 7.



meated by the gas, and the mercury in the diffusiometer-tube begins to fall, but it now falls slowly, owing to the considerable vacuous space to be filled. It is allowed to fall about half an inch, and the exact time is then noted, by a watch, when the mercury passes a certain point in the graduation of the tube, and again when the mercury descends to another fixed point an inch or two below the former. The time of permeation of a certain volume of gas is thus ascertained in seconds. The experiment is immediately repeated with two or more gases in succession, in similar circumstances as to pressure, and with great care taken to ensure uniformity of temperature during the whole period.

In a series of four experiments made with hydrogen, the mercury fell from 758 to 685 millims. (29·9 inches to 27 inches) in 252, 256, 254, and 256 seconds; mean, 254·5 seconds.

In three experiments with oxygen, the mercury fell through the same space in 1019, 1025, and 1024 seconds; mean, 1022·7 seconds:

$$\frac{1022{\cdot}7}{254{\cdot}5} = 4{\cdot}018$$

The times of these gases appear, therefore, to be 1 to 4·018, while the times calculated as being inversely as the square root of the densities of the same gases are as 1 to 4.

On another day, with a different height of the barometer, four gases were passed through the graphite plate in succession through a somewhat shorter range, namely, from 754 to 685 millims. (29·7 to 27 inches).

The time of permeation of air was 884 and 885 seconds; mean, 884·5 seconds.

The time of carbonic acid was 1100 and 1106 seconds; mean, 1103 seconds.

The time of oxygen was 936, 924, and 930 seconds; mean, 930 seconds.

The time of hydrogen was 229, 235, and 335 seconds; mean, 233 seconds.

These times of permeation are in the following proportion:—

| | Times of the permeation of equal volumes of gas through graphite. |
|---|---|
| Oxygen | 1 |
| Air | 0·9501 |
| Carbonic acid | 1·1860 |
| Hydrogen | 0·2505 |

These numbers approach so closely to the square roots of the density, or the theoretical diffusion-times of the same gases, namely, oxygen 1, air 0·9507, carbonic acid 1·176, and hydrogen 0·2502, that they may be held to indicate the prevalence of a common law. They exclude the idea of capillary transpiration, which gives to the same gases entirely different numbers.

The movement of gases through the graphite plate appears to be solely due to their own proper molecular motion, quite unaided by transpiration. It seems to be the simplest possible exhibition of the molecular or diffusive movement of gases. This pure result is to be ascribed to the wonderfully fine (minute) porosity of the graphite. The interstitial spaces appear to be sufficiently small to extinguish capillary transpiration entirely. The graphite plate is a pneumatic sieve which stops all gaseous matter in mass, and permits molecules only to pass.

It is worth observing what result a plate of more open structure, such as stucco, will give in comparison with graphite. For the graphite plate a cylinder of stucco, 12 millims. in thickness, was accordingly substituted, and gas allowed to percolate at both low and high pressures, as in the former experiments with graphite.

1. Under a constant pressure of 100 millims. of mercury, gas

was allowed to enter through 100 millim. divisions of the diffusiometer.

With air, the time in two experiments was 515, and again 515 seconds.

With hydrogen 178 seconds, and again 178 seconds:

$$\frac{515}{178} = 2{\cdot}891$$

2. Under a pressure beginning with 710 millims. (28 inches), and ending with 660 millims. (26 inches), the time with air was 374 and 375 seconds; mean 374·5 seconds. The time with hydrogen was 129 and 130 seconds; mean 129·5 seconds:

$$\frac{374{\cdot}5}{129{\cdot}5} = 2{\cdot}891$$

The stucco cylinder of the preceding experiments had been dried over sulphuric acid, without the application of heat. It was further dessicated at 60° C. for twenty-hours, in order to find whether the porosity would be altered. The ratio of the time of hydrogen to that of air now became 1 to 2·788 at the lower degree of pressure, and 1 to 2·744 at the higher degree of pressure.

It will be observed that the theoretical diffusion-ratio of hydrogen to air, which is as 1 to 3·80, is greatly departed from in these experiments with stucco. The ratio appears to be tending to the proportion of the transpiration-times of the same gases, namely, 1 to 2·01. In an experiment recorded by Bunsen, the ratio observed between the times of hydrogen and oxygen in passing, under a small degree of pressure, through stucco dried by heat, was so low as 1 to 2·73, the stucco being probably less dense than in the experiments before us.

With stucco the permeation of gases *under pressure* appears to be a mixed phenomenon—to some extent molecular diffusion into a vacuum, such as holds with the plate of graphite, but principally capillary transpiration of gas in mass.

The diffusiometer was now closed by a plate of white biscuitware, 2·2 millims. in thickness. The time of fall at the constant pressure of 100 millims., through a range of forty divisions of the diffusiometer, was, for air 1,210 seconds, for hydrogen 321 seconds.

$$\begin{array}{l} \text{Air} \ldots\ldots\ldots\ldots \\ \text{Hydrogen} \ldots\ldots \end{array} \quad \frac{1210}{321} = 3{\cdot}769.$$

The time, again, from 736 to 685 millims. (29 to 87 inches) was, for air, 685 and 684 seconds; mean 684·5 seconds; and for hydrogen, 183, 183, and 184 seconds; mean 183·3 seconds.

$$\begin{array}{l} \text{Air} \ldots\ldots\ldots\ldots \\ \text{Hydrogen} \ldots\ldots \end{array} \quad \frac{684{\cdot}5}{183{\cdot}5} = 3{\cdot}754.$$

The stoneware was evidently of a much closer texture than stucco, and the ratio appears again less influenced by capillary transpiration. In fact the molecular ratio of 1 to 3·80 is approached within 1 per cent. Biscuitware, therefore, appears to be but little inferior to graphite for such experiments, a circumstance which is important, as the latter is not easily procured, and cannot be converted into tubes and other convenient forms, like plastic clay.

Further, the rate of passage of gas through the plate of graphite appears to be closely proportional to the pressure. The resistance was increased by augmenting the thickness of the plate to 2 millims.; and with air and hydrogen at a pressure maintained constant at 50 and 100 millims., the time was observed that the gas took to enter 10 linear millimetre divisions of the tube.

| | Seconds. | Ratio. |
|---|---|---|
| Air under pressure of 100 millims. .... | 1925 | 1 |
| Air under pressure of 50 millims....... | 3880 | 2·015 |
| Hydrogen under pressure of 100 millims. | 497 | 1 |
| Hydrogen under pressure of 50 millims. | 1022 | 2·056 |

By halving the pressure, the time of passage is doubled, or increased somewhat more. Greater pressures might probably give a rate of passage corresponding more exactly with the pressure.

The ratio between the comparative times of the two gases in the last experiments may also be noticed, the observations having been made in similar circumstances as to pressure and temperature.

Barom. 760 millims.; Therm. 12°·9 C. At pressure of 50 millims.

$$\begin{array}{l} \text{Air} \ldots\ldots\ldots \\ \text{Hydrogen} \ldots \end{array} \quad \frac{3880}{1022} = 3{\cdot}796.$$

Barom. 760 millims.; Therm. 12°·9 C. At pressure of 100 millims.

$$\begin{array}{l} \text{Air} \ldots\ldots\ldots \\ \text{Hydrogen} \ldots \end{array} \quad \frac{1925}{497} = 3{\cdot}873.$$

The observation was repeated at the pressure of 100 millims., with barometer at 754 millims. and thermometer at 10° C.

$$\begin{array}{ll} \text{Air}\ldots\ldots\ldots\ldots & 1920 \\ \text{Hydrogen}\ldots\ldots & 498 \end{array} \quad \frac{1920}{498} = 3{\cdot}855.$$

The velocity of hydrogen appears, as usual, to be nearly 3·8 times that of air; $\frac{1}{\sqrt{0{\cdot}6926}} = 3{\cdot}7994$

An experiment was made at the same time as the former series upon a mixture of 95 hydrogen and 5 air, which gave an unlooked for result that led to a great deal of inquiry. It is known that such a mixture is effused through an aperture in a fine plate in a time which is as the square root of the density of the mixture, and therefore nearly the arithmetical mean of the two gases effused separately. But in transpiration by a capillary, a mixture of 95 hydrogen and 5 air requires a considerably longer time than the gases transpired separately. In fact 5 per cent. of air retards the transpiration of hydrogen nearly as much as 20 per cent. of air would retard the effusion of hydrogen.* Now the mixture in question permeates the graphite plate in 527·5 seconds, while the calculated mean of the times of the two gases is 562·1 seconds.

The mixture has therefore passed neither in the effusion time, nor in a longer time as it would do by capillary transpiration, but, singular to say, in a time considerably shorter than either. The gas that came through was found by analysis to be *altered in composition.* It contained more hydrogen and less air than the original mixture. Hence it passed through with increased rapidity. On consideration it appeared that such a separation of the mixed gases must follow as a consequence of the movement being molecular. Each gas is impelled by its own peculiar molecular force, which, as has been seen, is capable of causing hydrogen to permeate the graphite plate about 3·8 times as rapidly as air.

Each gas may permeate a graphite plate into a vacuum with the same relative velocity as it diffuses into another gaseous atmosphere, but it remains a question whether the velocities of permeation and diffusion are absolutely as well as relatively the same. To illustrate this point, hydrogen and air were first allowed to permeate into a vacuum, and then to diffuse into each other, through the same graphite plate, which was 1 millim. in thickness. The plate was a circular disc of 22 millims. in diameter.

---

* Philosophical Transactions, 1846, p. 628.

The mercurial column in the barometrical diffusiometer fell from 762 to 685 millims. (30 inches to 27) with air in 878 seconds, and with hydrogen in 233 seconds.

$$\begin{array}{ll} \text{Air} \ldots\ldots\ldots\ldots & 878 \\ \text{Hydrogen} \ldots\ldots & \overline{233} \end{array} = 3{\cdot}768.$$

The volume of gas which produced this effect was found by the calibration of the tube to be 8·85 cub. centims. Hence 1·22 cub. centim. of the hydrogen entered the diffusiometer in 60 seconds, or one minute. But the pressure under which the hydrogen gas entered was the mean of 762 to 685 millims., or 723·5 millims.; while a whole atmosphere (the height of the barometer at the time) was 765 millims. The volume of the gas has therefore to be increased as 723·5 to 765 to give the full action of a vacuum. The volume becomes 1·289 cub. centim. in one minute.

When the diffusiometer was filled with hydrogen and the gas allowed to diffuse into air, the rise of the mercury was pretty uniform for the first five minutes, being 15·5 millim. divisions in the first two minutes, 7 in the third minute, 7·5 in the fourth minute, and 7 in the fifth minute, making 37 divisions in five minutes. But as in diffusion, 1 air may be supposed to enter the tube for 3·8 hydrogen which escape, the hydrogen which diffused was more than 37 divisions, by $\frac{1}{3\cdot8}$, that is, by about 10 divisions. Hence 47 divisions of hydrogen have diffused into air in five minutes. These divisions measured, by the calibration of the tube, 6·215 cub. centims. One-fifth of this amount, that is, 1·243 cub. centims., diffused in one minute. The result of the whole is that in one minute there passed of hydrogen through the graphite plate,

1·289 cub. centim. by permeation into a vacuum,
1·243 cub. centim. by diffusion into air.

The numbers indicate a close approach to equality in the velocities of permeation into a vacuum and of diffusion into another gas, through the same porous diaphragm. The diffusion appears the slower of the two by a small amount; but this is as it should be, our estimate of the diffusion-velocity being certainly underrated; for the initial diffusion, or even the diffusion in the first minute, must obviously be somewhat greater than the average of the first five minutes, which we have taken to represent it—the hydrogen necessarily diffusing out in a diminishing progression, or more slowly in proportion as air has entered the diffusiometer. It is strictly the initial velocity of diffusion (that of the first second if it could be obtained) that ought to be compared with the percolation into a vacuum.

In fine, there can be little doubt left on the mind that the permeation through the graphite plate into a vacuum, and the diffusion into a gaseous atmosphere, through the same plate, are due to the same inherent mobility of the gaseous molecule. They are the exhibition of this movement in different circumstances. In interdiffusion we have two gases moved simultaneously through the passages in opposite directions, each gas under the influence of its own inherent force; while with gas on one side of the plate and a vacuum on the other side, we have a single gas moving in one direction only. The latter case may be assimilated to the former if the vacuum be supposed to represent an infinitely light gas. It will not involve any error, therefore, to speak of both movements as gaseous diffusion,—the diffusion of gas into gas (double diffusion) in one case, and the diffusion of gas into a vacuum (single diffusion) in the other. The inherent molecular mobility may also be justly spoken of as the diffusibility or diffusive force of gases.

The diffusive mobility of the gaseous molecule is a property of matter fundamental in its nature, and the source of many others. The rate of diffusibility of any gas has been said to be regulated by its specific gravity, the velocity of diffusion having been observed to vary inversely as the square root of the density of the gas. This is true, but not in the sense of the diffusibility being determined or *caused* by specific gravity. The physical basis is the molecular mobility. The degree of motion which the molecule possesses regulates the volume which the gas assumes, and is obviously one, if not the only, determining cause of the peculiar specific gravity which the gas enjoys. If it were possible to increase in a permanent manner the molecular motion of a gas, its specific gravity would be altered, and it would become a lighter gas. With the density is also associated the equivalent weight of a gaseous element, according to the doctrine of equal combining volumes.

### *Diffusion of mixed gases into a vacuum, with partial separation— Atmolysis.*

*Oxygen and Hydrogen.*—A diffusiometer of the same construction as that described (Fig. 3, p. 340), with a graphite plate of 1 millim. in thickness, was now employed. The upper surface of the plate was swept by a current of the mixed gas proceeding from a gas-holder, the excess of gas being allowed to escape into the atmosphere, as usual, by an open exit-tube. The gas was drawn through the graphite by elevating the diffusiometer containing a column of mercury, from its well, so as to command a partial vacuum in the upper part of the tube. Care is taken that any gas left in the upper part of the diffusiometer-tube before the experiment begins, should be of the same composition as the gas to be allowed afterwards to enter, so that, on starting, the gas may be uniform in composition on both sides of the graphite plate. The height of the mercurial column, which measures the aspirating force of the diffusiometer, is preserved uniform by gradually raising the tube in the mercurial trough in proportion as gas enters and the mercury falls. The diffusiometer is suspended from the roof of the apartment by a cord passing over a pulley and properly weighted, as in former experiments.

The mixture to be diffused consisted of nearly equal volumes of oxygen and hydrogen. The effect of different degrees of pressure on the amount of separation produced was first observed. It will be seen that, as the pressure or aspirating force is increased, the amount of separation becomes greater. Barom. 0·759 millim.; therm. 18°·3 C.

*Diffusion into a partial vacuum.*

| | Oxygen. | Hydrogen |
|---|---|---|
| Composition of original mixture in 100 parts .... | 49·3 | 50 7 |
| Diffused by pressure of 100 millims............ . | 47·0 | 53 |
| Diffused by pressure of 400 millims............. | 37·5 | 62·5 |
| Diffused by pressure of 673 millims. (mean of 635–710) ................................... | 26·4 | 73·6 |
| Diffused by pressure of 747 millims. (mean of 736–759) ......... ........................... | 22·8 | 77·2 |

In the last observation, or that with the greatest pressure (747 millims.), the oxygen is reduced to 22·8 per cent. and the hydrogen increased to 77·2 per cent. of the diffused mixture, showing a considerable separation. The mixed gases appear to make their way through the graphite plate independently, each following its own peculiar rate of diffusion.

But it is only under the aspiration of a complete vacuum, that the separation can attain its maximum, and reach the full difference that may exist between the special diffusibilities of the two gases. The reason is that, while we have the original mixture on both sides of the plate, and of equal tension, the gases are not at rest, but diffusion is proceeding as actively through the plate in opposite directions, as if the gases were different or the tension unequal on the two sides. This is a condition of the molecular mobility of gases (p. 336). The tension therefore being supposed to differ by 100 millims. only, as when the gas above the plate was of 759 millims. tension, and below of 659 millims. (in the first experiment of the last series), then 100 volumes only out of 759 of the mixture are subject to separation. But while these 100 volumes press through they are accompanied by 659 volumes of unchanged mixture. The latter 659 volumes are replaced by an equal bulk of unchanged mixture diffused from below, so that the volumes are not disturbed by this portion of the molecular interchange.

The amount of separation, then, attainable by transmitting a mixed gas through a porous diaphragm by pressure will be in proportion to the pressure—that is, to the inequality of tension on different sides of the diaphragm.

*Oxygen and Nitrogen.*—The separation of the gases of the atmosphere by transmission through the graphite plate has a peculiar interest.

In an experiment resembling those last described, atmospheric air was swept over the upper surface of a graphite plate having a thickness of 2 millims. The gas that penetrated into the vacuum contained, as was to be expected, the lighter and more diffusible constituent in excess. It gave by the pyrogallic acid and potash process of Liebig,

| | |
|---|---|
| Oxygen ............ | 20 |
| Nitrogen .......... | 80 |

This was an increase in the nitrogen of quite 1 per cent.; for air, analysed for comparison at the same time and in the same manner, gave oxygen 21·03 and nitrogen 78·97.

It may be legitimately inferred from the last experiment, that if pure hydrogen in a diffusiometer were allowed to diffuse into the atmosphere through a porous plate, the portion of air which then enters the diffusiometer should also have its composition disturbed. A diffusion of hydrogen through a graphite plate was interrupted before completion. The air which had entered was found to consist of

| | |
|---|---|
| Oxygen ...... .. | 19·77 |
| Nitrogen ....... | 80·23 |
| | 100·00 |

The increase of nitrogen is 1·23 per cent.

While the nitrogen is increased and the oxygen diminished in the air which makes its way under pressure through the graphite, the converse effect must be produced on the air left behind. But the latter result of atmolysis cannot be made apparent without a change in the mode of experimenting.

With the view of effecting an increase in the proportion of oxygen, a volume of air, confined in a jar suspended over mercury, was allowed to communicate through a graphite plate of 2 millims. in thickness, with a vacuum sustained by means of an air-pump, the guage being about 1 inch only below the height of the barometer during the whole time of experimenting.

The jar containing the air to be atmolysed was formed of a plain glass cylinder, open at both ends, and about 400 millims. in height (15·75· inches). The upper end was closed by a thick plate of gutta-percha cemented on. This plate was itself penetrated by a wide glass tube, descending about an inch into the jar. The last tube carried the graphite disc, which was 27 millims. (1·04 inch) in diameter, sufficient to close the lower end of the tube upon which it was cemented. The other or upper end of the same tube was fitted with a cork and quill tube, and was put into communication with a large bell jar upon the plate of the air-pump.

The permeation was slow, owing to the unusual thickness of the graphite plate, occupying three hours to drain away one-half of the original volume of air in the jar. The air remaining behind in the jar was examined in a series of experiments, in which the original volume was reduced to one-half, one-fourth, one-eighth, and one-sixteenth.

The residual air, reduced to one-half, gave in two experiments 21·4 and 21·57 per cent. of oxygen, the air of the atmosphere being by the same analytical process 21 per cent.

Reduced to one-fourth of its volume, the residual air gave, in two experiments, 21·95 and 22·01 per cent. of oxygen.

Reduced to one-eighth of its volume, the air gave 22·54 per cent. of oxygen.

Reduced to one-sixteenth of its volume, the air gave 23·02 per cent. of oxygen. The proportion of oxygen had therefore increased about one-tenth in the last experiment, where the effect is greatest.

When the numbers are compared, it appears that by a reduction to half its volume, the air gains about one-half per cent. of oxygen; when this last air is reduced to one-half again, another half per cent. of oxygen is gained, and so on—the gain in the proportion of oxygen increasing in an arithmetical ratio, while the volume of air is diminished in a geometrical ratio, or as the powers of the number 2.

| Reduction of one volume of air. | Proportion of oxygen per cent. | Increase of oxygen. |
|---|---|---|
| To 1 volume........ .. ... | 21 | 0 |
| To 0·5 volume ............ .. | 21·48 | 0·48 |
| To 0·25 volume...... ..... .. | 21·98 | 0·98 |
| To 0·125 volume .. ... ....... | 22·54 | 1·54 |
| To 0·0625 volume...... ........ | 23·02 | 2·02 |

The densities of oxygen and nitrogen approach too nearly to admit of any considerable separation being effected by this method. The density of oxygen being taken as 1, that of nitrogen is 0·8785. The square roots of these numbers are 1 and 0·9373, which are inversely as the diffusive velocity of the two gases.

| | Diffusive velocity. |
|---|---|
| Oxygen ........ | 1 |
| Nitrogen........ | 1·0669 |

The velocity of nitrogen therefore exceeds that of oxygen by about 6·7 per cent. Hence by a simple diffusion of a whole volume of air, the oxygen could only be increased 6·7 per cent., according to theory. In experiments such as the preceding, only one-half of the volume of the air is diffused, and consequently only one-half of the stated amount of concentration of oxygen could possibly be produced at each step. About three-fourths of the theoretical separation is actually obtained, although the apparatus works at an obvious disadvantage from the air within the jar being at rest.

This diffusive method of separation recalls the original observation of Döbereiner on the escape of hydrogen gas from a fissured jar standing over water, which will always hold its place in scientific history as the starting-point of the experimental study of gaseous diffusion. That observation proved to be an instance of double diffusion, air entering the jar by the fissure at the same time that hydrogen escaped by it—although, as Döbereiner looked upon the phenomenon, it was more akin to single diffusion or the passage of gas in one direction only.*

The atmolytic power of other diffusing plates was tested, besides the artificial graphite.

The barometrical diffusiometer already described was closed by a plate of *red unglazed earthenware,* 4 millims. in thickness, which was attached to the glass by resinous cement.

Dry air was swept over the upper surface, as in operating with the graphite plate. With a mercurial column of 340 millims. falling to 200 millims., the air which entered was found to contain 79·45 per cent. of nitrogen, instead of 79. With a column of mercury maintained at 508 millims. in the tube, the air entering contained 79·72 nitrogen, and with a column beginning at 761 millims., the full barometrical height, and falling to 679 millims. in seven minutes, the air entering contained 80·21 nitrogen. This is a full degree of separation, exceeding 1 per cent., while the time was greatly shorter than with graphite. Thermometer 19·5° C.

With a diffusing plate of gypsum (stucco) 10 millims. in thickness, the proportion of nitrogen was also increased, although less considerably than with biscuitware. The standard proportion of nitrogen observed in atmospheric air being 78·99 per cent., the air drawn into the diffusiometer was as follows:—

| | Proportion of nitrogen per cent. |
|---|---|
| In air entering over column of 330—200 millims. mercury | 79·26 |
| In air entering over column 508 millims. | 79·32 |
| In air entering over column 761—685 millims. | 79·53 |
| In air entering over column 761—685 millims. | 79·69 |

---

* Annales de Chimie, 1825.

The separation is sufficiently decided, and is certainly remarkable, considering the comparatively loose texture of the stucco plate. The gas entered in the two last experiments in about one minute, which appears too rapid a passage, and not to be attended with increased separation, compared with the immediately preceding experiment, in which the pressure was less and the passage of the gas proportionally slower. In all such highly porous plates, we have always to apprehend the passage of a large proportion of the gas in the manner of capillary transpiration, where no separation takes place.

It may be concluded that all porous masses, however loose their texture, will have some effect in separating mixed gases moving through them under pressure. The air entering a room by percolating through a wall of brick or a coat of plaster, will thus become richer in nitrogen, in a certain small measure, than the external atmosphere.

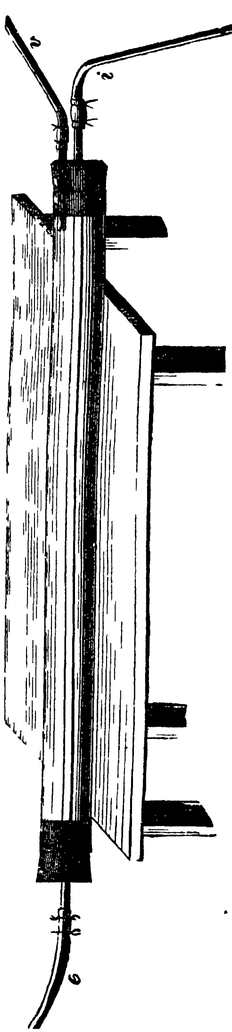


Fig. 8

### *The Tube Atmolyser.*

In the application of diffusion through a porous septum to separate mixed gases, as a practical analytical method, it is desirable that the process should be more rapid than it can be made with the use of graphite and other diffusing-plates of small size, and also that the process should if possible be a continuous one. Both objects are attained in a considerable degree by adapting a tube of porous earthenware to the purpose. Nothing has been found to answer better than the long stalk of a Dutch tobacco-pipe used as the porous tube. A tube of this description, about 2 feet long and having an internal diameter of 2·5 millims., is fixed by means of perforated corks within a glass or metallic tube, a few inches less in length; and about 1½ inch in diameter (*e*, *i*, fig. 8) as in the construction of a Liebig condenser. A second quill tube (*v*) is inserted in one of the end corks, and affords the means of communication between the annular space and the vacuum of an air-pump. The external surface of the corks, and of those portions of the pipe-stalk which project beyond the enclosing tube, should be coated with a resinous varnish, to render them impermeable to air. Now, a good vacuum being obtained within the outer tube, and sustained by the action of an air-pump, the mixed gas is made to enter and traverse the clay-tube. More or less of gas is drained off through the porous walls and pumped away, while a portion courses on and escapes by the other extremity of the clay tube, where it may be collected. The stream of gas diminishes as it proceeds, like a river flowing over a pervious bed. The lighter and more diffusive constituent of the mixed gases is drawn most largely into the vacuum, leaving the denser constituent, in a more concentrated condition, to escape by the exit end of the clay tube. The more slowly the mixed gas is moved through that tube, the larger the proportion of light gas that is drained off into the vacuum, and the more concentrated does the heavy gas become. The rate of flow of the mixed gas can be commanded by either discharging it from a gas-holder, or drawing it into a gas-receiver, in either case under a regulated pressure.

To observe the effect of a more or less rapid passage through the tube atmolyser, the impelling pressure was varied so as to allow a constant volume of half a litre of atmospheric air to pass through and be collected in different periods of time. The clay tube used in these particular experiments was not a tobacco-pipe, but a wide unglazed tube, about 431 millims. (17 inches) long, and 19 millims. (0·75 inch) in internal diameter. It was required to place so wide a tube in a vertical position, and to admit the air by the upper and draw it off by the lower extremity of the tube. The proportion of oxygen in the half-litre of air collected was as follows:—

| | Oxygen per cent. | | |
|---|---|---|---|
| | Experiment 1. | Experiment 2. | Mean. |
| When collected in 1 minute .... | 21·00 | .... | .... |
| When collected in 13 minutes.... | 22·33 | 22·25 | 22·29 |
| When collected in 75 minutes ... | 22·77 | 23·02 | 22·89 |
| When collected in 120 minutes ... | 23·25 | 23·22 | 22·23 |
| When collected in 304 minutes.... | 23·54 | 23·51 | 23·53 |

The proportion of oxygen in the air circulated, appears thus to increase with the slowness of its passage through the tube atmolyser. The proportion of air drawn into the air-pump vacuum must be very large when the time is protracted; but the additional concentration of oxygen appears small.

The preceding observations being made by means of a porous tube which may be considered wide and of considerable capacity with reference to its internal surface, the experiment was varied by substituting a porous tube about eight times as long, very narrow, and therefore of small internal capacity. This second atmolyser was composed of twelve ordinary tobacco-pipe stems, each about 10 inches in length and of 1·9 millim. internal diameter, connected together by vulcanised caoutchouc adapters, so as to form a single tube. Having flexible joints, the tube was folded up and placed within a glass cylinder that could be exhausted. Air was then circulated through this atmolyser by the pressure of several inches of water. The instrument appeared to work with most advantage when the air delivered at the exit-tube amounted to about one-fourth of a litre per hour. A volume of 268 cubic centrimetres, which had circulated in one hour, was found to contain 24·37 per cent. of oxygen. The current was then made slower, so that only 108 cub. centims. of gas passed and were collected in one hour, but with little further concentration of the oxygen. The result, however, is interesting, as being the highest concentration of oxygen yet obtained by an instrument of this kind. The air collected was composed of—

| | |
|---|---|
| Oxygen .......... | 24·52 |
| Nitrogen ........ | 75·48 |
| | 100·00 |

The increase of oxygen is 3·5 per cent.; that is, an increase of of 16·7 upon 100 oxygen originally present in the air.

With the single pipe-stalk, 24 inches long, first described, the oxygen of atmospheric air was concentrated about 2 per cent., when one litre was transmitted in one hour. Of 450 cub. centims. of air collected in that time, the composition proved to be

| | |
|---|---|
| Oxygen .......... | 23·12 |
| Nitrogen ........ | 76·88 |
| | 100·00 |

About 9 litres were drawn into the vacuum at the same time.

The separation of the gases of atmospheric air is a severe trial of the powers of the atmolyser, owing to the small difference in the specific gravities of these gases. But where a great disparity in density exists, the extent of the separation may become very considerable.

Several experiments were made upon a mixture of equal volumes of oxygen and hydrogen carried through the single tube atmolyser, 24 inches in length.

1. Of the mixture described, 7·5 litres entered the tube and 0·45 litre was collected in one experiment. The mixture was composed as follows:—

| | Oxygen. | | Hydrogen. |
|---|---|---|---|
| Before traversing the atmolyser .. | 50 | + | 50 |
| After traversing the atmolyser.... | 92·78 | + | 7·22 |

2. In another similar experiment, 14 litres of the mixed gas entered the tube and 0·45 litre was delivered in a period of two hours. The result was—

| | Oxygen. | | Hydrogen. |
|---|---|---|---|
| Before traversing the atmolyser .. | 50 | + | 50 |
| After traversing the atmolyser.... | 95 | + | 5 |

Here the proportion of hydrogen is reduced from 50 to 5 per cent.

3. Of the explosive mixture, consisting of 1 volume oxygen and 2 volumes hydrogen, 9 litres were transmitted and 0·45 litre collected in one hour. The change effected was found to be as follows:—

| | Oxygen. | | Hydrogen. |
|---|---|---|---|
| Before traversing the atmolyser .. | 33·33 | + | 66·66 |
| After traversing the atmolyser.... | 90·7 | + | 9·3 |

The result in such experiments is striking, as the gas ceases to be explosive after traversing the porous tube, and a lighted taper burns in it as in pure oxygen. A mixture of oxygen and hydrogen is not explosive till the hydrogen rises to 11 per cent.

To illustrate the analogy of diffusion into a vacuum with diffusion into air, the outer glass tube of the diffuser was now withdrawn, and the porous tube of the instrument was exposed directly to the air of the atmosphere. A mixture of equal volumes of oxygen and hydrogen was again transmitted at the same rate of velocity as in experiment 1.

The gas atmolysed and collected was found to consist of—

| | |
|---|---|
| Oxygen .......... | 51·75 |
| Hydrogen ........ | 5·47 |
| Nitrogen ........ | 42·78 |
| | 100·00 |

And may be represented as containing—

| | |
|---|---|
| Oxygen .......... | 40·38 |
| Hydrogen ........ | 5·47 |
| Air.............. | 54·15 |
| | 100·00 |

A nearly similar concentration of the oxygen of the mixed gas is here observed, as appeared in experiment 1; but the gas collected is now diluted with air, which has entered by diffusion. The external air manifestly discharges the same function in the latter experiment which the air-pump vacuum discharged in the former experiment.

### *Interdiffusion of Gases—Double Diffusion.*

The diffusiometer was much improved in construction by Professor Bunsen, from the application of a lever arrangement to raise and depress the tube in the mercurial trough; but the mass of stucco forming the porous plate in his instrument appears too voluminous, and, from being dried by heat, is liable to detach itself from the walls of the glass tube. The result obtained of 3·4 for hydrogen, which diverges so far from the theoretical number, is, however, no longer insisted upon by that illustrious physicist. It is indeed curious that my old experiments generally rather exceeded than fell short of the theoretical number for hydrogen; $\sqrt{0{\cdot}06926} = 3{\cdot}7994$. With stucco as the material, the cavities existing in the porous plate form about one-fourth of its whole bulk, and affect sensibly the ratio in question, according as they are or are not included in the capacity of the instrument. Beginning the diffusion always with these cavities, as well as the tube, filled with hydrogen, the numbers now obtained with a stucco plate of 12 millims. in thickness and dried without heat, were 3·783, 3·8, and 3·739 when the volume of the cavities of the stucco is added to both the air and hydrogen volumes diffused; and 3·931, 3·949, and 3·883 when such addition is not made to these volumes. The graphite plate, on the other hand, being very thin, and the volume of its pores too minute to require to be taken into account, its action is not attended with the same uncertainty. With a graphite plate of 2 millims. in thickness, the number for hydrogen into air was 3·876, instead of 3·8; and for hydrogen into oxygen 4·124, instead of 4. With a graphite plate of 1 millim. in thickness, hydrogen gave 3·993 to air 1. With a plate of the same material 0·5 millim. in thickness, the proportional number for hydrogen to air rose to 3·984, 4·068, and 4·067. An equally considerable departure from the theoretical number was observed when hydrogen was diffused into oxygen or into carbonic acid, instead of air. All these experiments were made with dry gases and over mercury. It appears that the numbers are most in accordance with theory when the graphite plate is thick, and the diffusion slow in consequence. If the diffusion be very rapid, as it is with the thin plates, something like a current is possibly formed within the channels of the graphite, taking the direction of the hydrogen, and carrying back in masses a little air, or the slower gas, whatever it may be. I cannot account otherwise for the slight predominance which the lighter and faster gas appears always to acquire in diffusing through the porous septum.

### *Interdiffusion of Gases without an intervening septum.*

The relative velocity with which different gases diffuse is shown by the diffusiometer, but the absolute velocity of the molecular movement cannot be ascertained by the same instrument. For that purpose it appears requisite that a gas should be allowed to diffuse into air through a wide opening.

In certain recent experiments, a heavy gas, such as carbonic acid, was allowed to rise by diffusion into a cylindrical column of air, pretty much as the saline solution is allowed to rise into a column of water in my late experiments upon the diffusion of liquids. This method of gaseous diffusion appears to admit of considerable precision, and deserves to be pursued further. A glass cylinder of 0·57 metre (22·44 inches) in height had the lower tenth part of its volume occupied with carbonic acid, and the upper nine-tenths with air, in a succession of experiments: thermometer 16° cent. After the lapse of a certain number of minutes, the upper tenth part of the volume was drawn off from the top of the jar and examined for carbonic acid. Before the carbonic acid appeared above, it had ascended, that is, it had diffused, a distance of 0·513 metre, or rather more than half a metre. After the lapse of five minutes, the carbonic acid so found in two experiments amounted to 0·4 and 0·32 per cent. respectively. In 7 minutes, the carbonic acid observed was 1·02 and 0·90 per cent.; mean 0·96 per cent. The effect of diffusion is now quite sensible, and it may be said that about 1 per cent. of carbonic acid has diffused to a distance of half a metre in seven minutes.

A portion of carbonic acid has therefore travelled by diffusion at an average rate of 73 millims. per minute. It may be added that hydrogen was found to diffuse downwards, in air contained in the same cylindrical jar, at the rate of 350 millims. per minute, or about five times as rapidly as the carbonic acid ascended. In these experiments the glass cylinder was loosely packed with cotton wool, to impede the action of currents in the column of air; but this precaution was found to be unnecessary, as similar results were afterwards obtained in the absence of the cotton. To illustrate the regularity of the results, I may complete this statement by exhibiting the proportion of carbonic acid found in the upper stratum already referred to, after the lapse of different periods of time.

| | Carbonic acid per cent. | | |
|---|---|---|---|
| | Experiment 1. | Experiment 2. | Mean. |
| After 5 minutes ........ | 0·4 | 0·32 | 0·36 |
| After 7 minutes ........ | 1·02 | 0·90 | 0·96 |
| After 10 minutes ........ | 1·47 | 1·56 | 1·51 |
| After 15 minutes ........ | 1·70 | 1·68 | 1·69 |
| After 20 minutes ........ | 2·41 | 2·69 | 2·55 |
| After 40 minutes ........ | 5·60 | 5·15 | 5·37 |
| After 80 minutes ........ | 8·68 | 8·82 | 8·75 |

In eighty minutes the proportion of carbonic acid had risen to 8·75 per cent., 10 per cent. being the proportion which would indicate the completion of the process of diffusion.

The same intestine movement must always prevail in the air of the atmosphere, and with even greater velocity, in the proportion of 1 to 1·176, the relative diffusion-ratios of carbonic acid and air. It is certainly remarkable that in perfectly still air its molecules should spontaneously alter their position, and move to a distance of half a metre, in any direction, in the course of five or six minutes. The molecules of hydrogen gas disperse themselves to the distance of a third of a metre in a single minute. Such a molecular movement may become an agency of considerable power in distributing heat through a volume of gas. It appears to account for the high convective power observed in hydrogen, the most diffusive of gases.

## XXXIX.—*On the Action of Hydrogen on Organic Polycyanides.*

By T. Fairley.

Mendius has shown that the cyanides of the monatomic alcohol-radicles can absorb four atoms of hydrogen to give the monamine containing the radicle one step higher in the series. It is known that these cyanides are also the nitriles of the monobasic acids, which can be regenerated from them by the action of strong acids or alkalies. Maxwell Simpson has proved that the cyanides of the glycol radicles are the nitriles of the bibasic acids, which can be regenerated from them by similar means.

It seemed to me interesting to determine whether this similarity, which has been proved between the mono- and poly-cyanides in their reactions with water, was also maintained in their reactions with hydrogen.

The first experiment was performed with cyanogen or oxalonitrile. Mendius' reaction being expressed by the equation—

$$HCN + H_4 = CH_3H_2N, \text{ or } CH_5N.$$

the transformation of cyanogen should be thus expressed :—

$$C_2N_2 + H_8 = C_2H_4H_4N_2 = C_2H_8N_2.$$

and this body $C_2H_8N_2$ should, according to the analogies of the case, be identical with the base described by Cloez, and by Natanson under the name acetylia, and by Hofmann under the more correct name of ethylene-diamine.

*Cyanogen* was acted on by tin and hydrochloric acid. The tin was precipitated by sulphuretted hydrogen, and the liquid evaporated. To the solution of the white residue obtained, I added soluble chloride of platinum, which gave a crystalline precipitate, soluble in hot water, less so in cold water, and still more sparingly soluble in alcohol.

0·4687 grm. of salt gave 0·1957 of Pt, which corresponds to 41·77 per cent. The formula $C_2H_{10}N_2Pt_2Cl_6$ requires 41·79 per cent.

A portion of the supposed chloride of ethylene-diammonium distilled with soda-ley gave a strongly alkaline liquid not boiling under 100° C, but the distillate was too small in quantity and dilute to determine the boiling point strictly. Ethylene-diamine boils at 118° C.

That the base does not boil under 100° C shows that it cannot be methylamine, which is a gas, but whose platinum percentage corresponds very closely with the above. It might also relate from the equation :

$$C_2N_2 + H_{10} = 2CH_5N.$$

*Cyanide of ethylene*, subjected to a similar process, gave a like result. Its equation is : —

$$C_2H_4C_2N_2 + H_8 = \underbrace{C_4H_8H_4N_2}_{\text{Butylene-diamine.}} = C_4H_{12}N_2.$$

The chloride obtained was very soluble in water and somewhat deliquescent. Its solution in hot alcohol gave small brilliant crystals on cooling. On adding bichloride of platinum to their solution, small crystalline grains of the chloroplatinate were obtained. Their analysis gave 39·43 per cent. of Pb. The formula $C_4H_{14}N_2Pt_2Cl_6$ requires 39·45.

A portion of the chloride distilled with soda-ley gave a strongly alkaline distillate not boiling under 140° C.

I will afterwards publish a more detailed investigation of this series of bases.

*Cyanoform.* I have made cyanoform by heating chloroform with cyanide of potassium and some alcohol in soda-water bottles to 100° C. It has not been made before. At 100° C it is a thick, apparently non-volatile liquid, of a peculiar smell, which solidifies to a thick pasty mass at ordinary temperatures. It is the example of a tricyanide which I have selected. Triatomic cyanides should take up twelve atoms of hydrogen; the equation for cyanoform is therefore :—

$$CH.C_3N_3 + H_{12} = C_4H_7.H_6N_3,$$

and for this base I propose the name tetryline-triamine—the triatomic radicle $C_4H_7$ being called *tetryline.* The hydrate of this radicle would be the hypothetical butylic glycerin.

I succeeded in obtaining the chloride of a base, which gave a chlorplatinate, whose analysis agreed within half a per cent. with that required by the formula $C_4H_{16}N_3Pt_3Cl_9$. This chlorplatinate was in small crystals. No precautions were taken to purify the chloride from which it was prepared.

This chloride crystallizes, but not distinctly. When distilled with soda-ley, it gave a strongly alkaline liquid, of a peculiar pungent smell. I took no precautions to purify the distillate, but it did not begin to boil under 150° C.*

I intend to show the perfectly general nature of Mendius' reaction, and that the greater number of cyanogen-compounds which it is possible to form, will absorb four atoms of hydrogen for each atom of cyanogen which they contain, to form corresponding bases.

For this end I will take examples of all the organic chlorides and *chlorine substitution* products, and attempt their conversion into corresponding cyanides and these last into corresponding bases.

The cyanide of an $x$-atomic radical will yield an $x$-amine thus :—

$$C_nH_{2n+1-p}.(CN)_x + H_{4x} = C_{n+x}H_{2(n+2x)+1-p}N_x,$$

and the constitution of this $x$-amine would be :—

$$\left.\begin{matrix} C_{n+x}H_{2(n+x)+1-p} \\ H_{2x} \end{matrix}\right\} N_x$$

---

* Cyanoform should give an acid $C_4H_4O_6 = C_4HO_3.3HO$. I used all I prepared at first in making the base, but I am now engaged in making it in larger quantity, and hope to get this new acid

In the case of cyanide of ethyl, $n = 2$, $p = 0$, $x = 1$, and we therefore get propylamine, $C_3H_9N = C_3H_7.H_2N$.

For cyanogen, $n = 0$, $x = 2$ and $p = 1$, and therefore we have, the body $C_2H_8N_2 = C_2H_4.H_4N_2$.

For cyanoform, $n = 1$, $x = 3$, $p = 2$, and therefore we have

$$C_4H_{13}N_3 = C_4H_7.H_6N_3.$$

Similarly for other cyanides.

Kolbe and Hugo Müller have shown that cyanacetic acid reacts with the elements of water to form malonic acid. Hugo Müller observes that there thus seems to be an intermediate step in the conversion of biatomic cyanides into the bibasic acids. Thus:—

Cyanide of ethylene $= C_2H_4.C_2N_2$.
Cyanopropionic acid $= C_3H_4.CNHO_2$.
Succinic acid $= C_4H_6O_4$;

and I would add that, with a poly-cyanide containing $n$ atoms of cyanogen, there would be $n$ steps altogether, and therefore $n - 1$ intermediate steps.

From this it may be inferred that the hydrogenation of these cyanides may take place by successive stages. Thus:—

Cyanide of ethylene $C_2H_4.C_2N_2$.

Cyanopropylamine $= C_3H_7.CN.HN = \left.\begin{matrix} C_3H_7 \\ CN \\ H \end{matrix}\right\} N.$

Butylene-diamine $C_4H_8.H_4N_2 = \left.\begin{matrix} C_4H_8{}'' \\ H_4 \end{matrix}\right\} N_2,$

or with cyanoform, we should have:—

Cyanoform $CH.C_3N_3$.

Dicyanethylamine $C_2H_5(CN)_2N = \left.\begin{matrix} C_2H_5 \\ (CN)_2 \end{matrix}\right\} N.$

Cyanopropylenediamine $C_3H_6.CNH_3N_2 = \left.\begin{matrix} C_3H_6{}'' \\ CN \\ H_3 \end{matrix}\right\} N_2.$

Tetryline-triamine $C_4H_7.H_6N_3 = \left.\begin{matrix} C_4H_7{}''' \\ H_6 \end{matrix}\right\} N_3.$

&c. &c.

As the hydrogenizing process is not under control, the existence of these intermediate steps must be shown otherwise than by stopping the process at any particular moment. The best means seems to be the use of chloride of cyanogen. Its action on ethylamine is:—

$$C_2H_5.H_2N + CNCl = HCl + C_2H_5.CN.HN,$$

or generally:—

$$C_nH_{2(n-p)+1}.H_2N + CNCl = HCl + C_nH_{2(n-p)+1}.CN.HN,$$

and the fact that cyanopropylamine, thus obtained, is an intermediate step in the conversion of bicyanide of ethylene into butylene-diamine will be proved, if we can succeed in hydrogenizing cyanopropylamine into butylene-diamine.

This is a general method, and by its means we may convert any amine $x$-atomic into an amine, $x + 1$ atomic. Thus:—(See formula on last page.)

$$\left.\begin{matrix} C_{n+x}H_{2(n+x)+1-p} \\ H_{2x} \end{matrix}\right\} N_x \text{ into } \left.\begin{matrix} C_{n+x+1}H_{2(n+x+1)-p} \\ H_{2x+2} \end{matrix}\right\} N_{x+1}$$

## XL.—*Note on the action of Chloride of Iodine on certain Organic Substances.*

By JOHN STENHOUSE, LL.D., F.R.S., &c.

OWING to an inadvertence, the mean of the analyses (p. 330) was omitted. It should have been as follows:—

| | Mean |
|---|---|
| C | 15·66 |
| H | 1·07 |
| I | 66·23 |
| N | 3·22 |
| O | 13·82 |
| | 100·00 |

# XLI.—*On a Curious Example of Etherification.*

By J. Alfred Wanklyn.

Some years ago Frankland showed that iodide of ethyl and water yield hydriodic acid and ether, on being exposed to the action of a temperature of 150° C. under pressure:

$$2C_2H_5I + H_2O = (C_2H_5)_2O + 2HI.$$

I have recently observed a somewhat similar reaction which, however, takes place at temperatures so low as 100° C.

When rosaniline, iodide of ethyl, and alcohol are heated together to 100°C. for about twelve hours, there is formed, in addition to the iodide of ethyl-rosaniline, a quantity of common ether. The production of this ether may be explained as follows:—

The three atoms of hydriodic acid resulting from reaction between three atoms of iodide of ethyl and one atom of rosaniline are thus appropriated; one atom goes to saturate the ethyl-rosaniline, and the remaining two react upon the alcohol:

$$2HI + 2C_2H_6O = 2HI + H_2O + (C_2H_5)_2O.$$

Or, we may suppose that the production of ether takes place quite directly:

$$C_2H_5I + C_2H_6O = HI + (C_2H_5)_2O.$$

Whichever way we regard the reaction, the fact is deserving of attention. Reasoning upon it, we should be led to expect the production of ether in the process for the preparation of the ethylated ammonias, *i.e.*, when we heat iodide of ethyl with alcoholic solution of ammonia. Common ether is likewise to be looked for in the preparation of various compound ethers by digesting different salts with iodide of ethyl and alcohol.

I am informed that this formation of ether as a bye-product in the manufacture of ethylated rosaniline, has also been noticed by continental manufacturers.

## XLII.—*Speculative Ideas respecting the Constitution of Matter.*

### By T. GRAHAM, F.R.S.

IT is concivable that the various kinds of matter, now recognised as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies. We know the anxiety with which this point was investigated by Newton, and the care he took to ascertain that every kind of substance, "metals, stones, woods, grain, salts, animal substances, &c.," are similarly accelerated in falling, and are therefore equally heavy.

In the condition of gas, matter is deprived of numerous and varying properties, with which it appears invested when in the form of a liquid or solid. The gas exhibits only a few grand and simple features. These again may all be dependent upon atomic and molecular mobility. Let us imagine one kind of substance only to exist, ponderable matter; and further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall then have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement, the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific motion of an atom being inalienable, light matter is no longer convertible into heavy matter. In short, matter of different density forms different substances—different inconvertible elements as they have been considered.

What has already been said is not meant to apply to the gaseous volumes which we have occasion to measure and practically deal with, but to a lower order of molecules or atoms. The combining atoms hitherto spoken of are not therefore the molecules, of which the movement is sensibly affected by heat, with gaseous expansion as the result. The gaseous molecule must itself be viewed as composed of a group or system of the preceding inferior atoms, following as a unit, laws similar to those which regulate its constituent atoms. We have indeed carried one step backward, and applied to the lower orders of atoms, ideas suggested by the gaseous molecule, as views derived from the solar system are extended to the subordinate system of a planet and its satellites. The advance of science may further require an indefinite repetition of such steps of molecular division. The gaseous molecule is then a reproduction of the inferior atom on a higher scale. The molecule or system is reached which is affected by heat, the diffusive molecule, of which the movement is the subject of observation and measurement. The diffusive molecules are also to be supposed uniform in weight, but to vary in velocity of movement, in correspondence with their constituent atoms. Accordingly the molecular volumes of different elementary substances have the same relation to each other as the subordinate atomic volumes of the same substances.

But further, these more and less mobile, or light and heavy forms of matter, have a singular relation connected with equality of volume. Equal volumes of two of them can coalesce together, unite their movement, and form a new atomic group, retaining the whole, the half, or some simple proportion of the original movement and consequent volume. This is chemical combination. It is directly an affair of volume, and only indirectly connected with weight. Combining weights are different, because the densities, atomic and molecular, are different. The volume of combination is uniform, but the fluids measured vary in density. This fixed combining measure—the *metron* of simple substances—weighs 1 for hydrogen, 16 for oxygen, and so on with the other "elements."

To the preceding statements respecting atomic and molecular mobility, it remains to be added that the hypothesis admits of another expression. As in the theory of light we have the alternative hypotheses of emission and undulation, so in molecular mobility the motion may be assumed to reside either in separate atoms and molecules, or in a fluid medium caused to undulate. A special rate of vibration or pulsation originally imparted to a portion of the fluid medium enlivens that portion of matter with an individual existence, and constitutes it a distinct substance or element.

With respect to the different stages of gas, liquid and solid, it may be observed that there is no real incompatibility with each other in these physical conditions. They are often found together in the same substance. The liquid and the solid conditions supervene upon the gaseous condition rather than supersede it. Gay-Lussac made the remarkable observation that the vapours emitted by ice and water, both at 0° C., are of exactly equal tension. The passage from the liquid to the solid state is not made apparent in the volatility of water. The liquid and solid conditions do not appear as the extinction or suppression of the gaseous condition, but something *superadded* to that condition. The three conditions (or constitutions) probably always coexist in every liquid or solid substance, but one predominates over the others. In the general properties of matter we have, indeed, to include still further (1) the remarkable loss of elasticity in vapours under great pressure, which is distinguished by Mr. Faraday as the Caignard-Latour state, after the name of its discoverer, and is now undergoing an investigation by Dr. Andrews, which may be expected to throw much light upon its nature; (2) the colloidal condition or constitution, which intervenes between the liquid and crystalline states, extending into both, and affecting probably all kinds of solid and liquid matter in a greater or less degree. The predominance of a certain physical state in a substance appears to be a distinction of a kind with those distinctions recognised in natural history as being produced by unequal development. Liquefaction or solidification may not therefore involve the suppression of either the atomic or the molecular movement, but only the restriction of its range.' The hypothesis of atomic movement has been elsewhere assumed, irrespective of the gaseous condition, and is applied by Dr. Williamson to the elucidation of a remarkable class of chemical reactions which have their seat in a mixed liquid.

Lastly, molecular or diffusive mobility has an obvious bearing upon the communication of heat to gases by contact with liquid or solid surfaces. The impact of the gaseous molecule, upon a surface possessing a different temperature, appears to be the condition for the transference of heat, or the heat movement, from one to the other. The more rapid the molecular movement of the gas, the more frequent the contact with consequent communication of heat. Hence, probably, the great cooling power of hydrogen gas as compared with air or oxygen. The gases named have the same specific heat for equal volumes, but a hot object placed in hydrogen is really *touched* 3·8 times more frequently than it would be if placed in air, and 4 times more frequently than it would be if placed in an atmosphere of oxygen gas. Dalton had already ascribed this peculiarity of hydrogen to the high "mobility" of that gas. The same molecular property of hydrogen recommends the application of that gas in the air-engine, where the object is to alternately heat and cool a confined volume of gas with rapidity.

## XLIII.—*On the Action of Sodium on Valerianate of Ethyl, viz., the Liberation of the Acid-forming Radicle Valeryl.*

By J. ALFRED WANKLYN.

MORE than twenty years ago an account of some experiments on the action of potassium upon acetic ether was published by Löwig and Weidmann.*

The result arrived at was that potassium reacts very energetically upon acetic ether, but that no gas is produced. The solid products were, moreover, found to consist partly of ethylate of potash, and partly of the potash-salt of a curious acid closely related to acetic acid, but which was only slightly examined.

This research does not appear to have attracted much attention. It was at the time unintelligible; and later, when the classical researches of Frankland and Kolbe, relating to the alcohol-radicles, came out, it seemed not to be in harmony with them. Inasmuch as metals eliminate ethyl from iodide of ethyl, it was not unnatural to suppose that they would also eliminate ethyl from acetate of ethyl and from other salts of ethyl.

In undertaking an investigation of the action of sodium upon the ethers of the fatty acids, the first point demanding attention was whether it is really a fact that the metal does not liberate the alcohol-radicle.

I have made very careful experiments on acetate of ethyl and on valerianate of ethyl, and get results corresponding in this particular with those of Löwig and Weidmann.

I sealed up a quantity of sodium with acetate of ethyl, which had been very carefully deprived of alcohol and of water, and weighed the tube containing these materials. I then heated the tube to 130° C for some time, until the contents had changed from liquid to solid. After opening the tube and allowing any gas that might have formed to escape, I weighed it again. The loss amounted to 0·5 in 100 parts of acetic ether. Therefore no appreciable quantity of gas is evolved in the reaction of sodium upon acetate of ethyl, and, therefore, sodium does not react upon acetate of ethyl in the manner represented by this equation—

---

* Ann Ch. Pharm., xxxvi, 297.

$$2\,.\left.\begin{array}{l}C_2H_3O\\C_2H_5\end{array}\right\}O + Na_2 = 2.\left.\begin{array}{r}C_2H_3O\\Na\end{array}\right\}O + \left.\begin{array}{r}C_2H_5\\C_2H_5\end{array}\right\}$$

This result was confirmed in various ways. With sodium and valerianic ether, unquestionable results of a like character were also obtained.

If we consider what is really known about acetate of ethyl, we shall find that after all it is not so very clear that ethyl is the moveable portion in it.

The reaction between acetate of ethyl and caustic potash, whereby alcohol is formed, is capable of two explanations, viz. :—

$$(1)\ldots\left.\begin{array}{l}C_2H_3O\\\cancel{C_2H_5}\end{array}\right\}O + \left.\begin{array}{l}H\\\cancel{K}\end{array}\right\}O = \left.\begin{array}{r}C_2H_3O\\K\end{array}\right\}O + \left.\begin{array}{r}H\\C_2H_5\end{array}\right\}O,*$$

wherein ethyl and potassium change against one another.

$$(2)\ldots\left.\begin{array}{l}\cancel{C_2H_3O}\\C_2H_5\end{array}\right\}O + \left.\begin{array}{l}\cancel{H}\\K\end{array}\right\}O = \left.\begin{array}{l}H\\C_2H_5\end{array}\right\}O + \left.\begin{array}{r}C_2H_3O\\K\end{array}\right\}O,$$

wherein acetyl and hydrogen change against one another.

The remarkable fact discovered by Beilstein, that acetic ether does not give ether by reaction with ethylate of sodium, but forms with it a double compound, which splits up, on the addition of water, into alcohol and acetate of soda, points to a fundamental want of resemblance between the ethers of the fatty acids and the haloid ethers, such as the iodides.

The well known reaction

$$\left.\begin{array}{r}C_2H_5\\I\end{array}\right\} + \left.\begin{array}{l}Na\\C_2H_5\end{array}\right\}O = \left.\begin{array}{r}Na\\I\end{array}\right\} + \left.\begin{array}{r}C_2H_5\\C_2H_5\end{array}\right\}O,$$

is thus seen to be without its counterpart when acetic ether is taken, the reaction

$$\left.\begin{array}{l}C_2H_5\\C_2H_3O\end{array}\right\}O + \left.\begin{array}{l}Na\\C_2H_5\end{array}\right\}O = \left.\begin{array}{l}Na\\C_2H_5O\end{array}\right\}O + \left.\begin{array}{r}C_2H_5\\C_2H_5\end{array}\right\}O$$

being found not to take place.

---

* The radicles which are supposed to replace one another are *crossed*.

If we allow that in acetic ether it is the acetyl, and not the ethyl which is moveable, then it is clear that acetic ether and ethylate of sodium cannot react so as to produce a change in the product:

$$\left.\begin{matrix}\cancel{C_2H_3O}\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}\cancel{Na}\\ C_2H_5\end{matrix}\right\}O = \left.\begin{matrix}Na\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O,$$

giving ethylate of sodium and acetic ether, the very compounds which were taken at first.

Many other facts which are familiar to chemists tend in the same direction; the uniformity with which an acetate of a radicle gives the alcohol when it is treated with potash is one of them.

This is particularly striking in the $\beta$ Hexyl series :—

Iodide of $\beta$ hexyl gives hexylene with alcoholic potash. Acetate of $\beta$ hexyl gives no trace of hexylene, but $\beta$ hexylic alcohol instead:

$$\left.\begin{matrix}C_2H_3O\\ \beta C_6H_{13}\end{matrix}\right\}O + \left.\begin{matrix}H\\ K\end{matrix}\right\}O = \left.\begin{matrix}H\\ \beta C_6H_{13}\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\}O,$$

where the reaction is confined to an interchange between acetyl and hydrogen, and where, the $\beta$ hexyl being undisturbed, it has little opportunity for the display of its characteristic tendency to split up into hydrogen and hexylene.

Another remarkable reaction which favours the interpretation for which I am contending, is that between ammonia—even aqueous solution of ammonia—and an ether of a fatty acid, *e.g.*:—

$$\left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\ NH_2\end{matrix}\right\} = \left.\begin{matrix}H\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ NH_2\end{matrix}\right\}$$

wherein acetic ether and ammonia give rise to alcohol and acetamide, acetyl changing against hydrogen, and not ethyl against ammonium.

After these examples of the mobility of acetyl, the following equations will not appear to be contrary to analogy:—

$$(1)\ldots.\ 2.\ \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + Na_2 = 2.\ \left.\begin{matrix}Na\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}.$$

$$(2)\ldots.\ 2.\ \left.\begin{matrix}C_5H_9O\\ C_2H_5\end{matrix}\right\}O + Na_2 = 2.\ \left.\begin{matrix}Na\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_5H_9O\\ C_5H_9O\end{matrix}\right\}$$

For obvious reasons, it is easier to investigate the action of sodium upon valerianic ether than upon acetic ether. The advantage in dealing with a case when there is a difference in carbon-condensation between the acid-forming radicle and the alcohol-forming radicle, as in valerianic ether, over a case where, as in acetic ether, both radicles are alike in carbon-condensation, will be at once apparent.

On the present occasion, therefore, I shall give in detail an account of the examination of the action of sodium on valerianic ether, reserving the investigation of acetic ether and other ethers for a future opportunity.

The valerianic ether used in this research, after being washed and dried, boiled constantly between 132° and 135° C. A portion was digested in a sealed tube with aqueous solution of potash; it dissolved completely in the potash, leaving no oily layer.

On placing pieces of sodium in valerianic ether, the metal becomes very bright, and assumes a yellowish colour, like gold; heat is developed, but there is no evolution of gas. Bye and bye the liquid becomes very thick, a white solid being formed, and the reaction seems to come to a stand-still on account of the extreme viscidity of the product.

In order to obtain anything like a complete reaction, it was necessary to employ some inert liquid to act as a diluent. Ether was chosen for this purpose, and before being used was washed with water, to remove any alcohol, and very completely dried, first with potash, and afterwards by distillation off fragments of metallic sodium.

The following are the details of an experiment—

2 grms. of sodium,
6 grms. of valerianic ether,
7·5 grms. of ether,

were sealed up together and heated in the water-bath. After the whole contents of the tube had become very thick—almost solid—the tube was opened, and the sodium unacted upon was cleaned and weighed. It weighed 0·7 grm. The amount of sodium which had taken part in the reaction was, therefore, 1·3 grm.

The product from which the unattacked sodium had been separated was next treated with water, when it yielded an oil and an aqueous layer which was strongly alkaline. The amount of free alkali, estimated by means of a standard solution of acid, corresponded to 1·08 grm. of sodium.

The oil, which of course contained large quantities of ether, was washed, then heated in an open vessel in the water-bath to drive off the ether, then transferred to a little bottle and weighed. After this operation it weighed 2·2 grm.

It was dried and burnt with oxide of copper, a little chlorate of potash being used.

·2680 grm. gave ·7024 grm. $CO_2$ and ·2815 grm. $H_2O$.

| | |
|---|---|
| Carbon...... | 71·48 |
| Hydrogen.... | 11·67 |
| Oxygen...... | 16·85 |
| | 100·00 |

Therefore, grms.

Valerianic ether taken = 6
Sodium consumed = 1·3
Sodium in caustic state = 1·08
Oily product = 2·2

The equation

$$2.\ \left.\begin{matrix}C_5H_9O\\ C_2H_5\end{matrix}\right\}O + Na_2 = 2.\ \left.\begin{matrix}Na\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_5H_9O\\ C_5H_9O\end{matrix}\right\}$$

requires:— grms.

Valerianic ether taken = 6
Sodium consumed = 1·06
Sodium in caustic state = 1·06
Valeryl = 3·92

It will be seen that the amount of sodium found in the caustic state is almost the theoretical quantity, and the remark may be made that the method by which this datum is arrived at is calculated to give a precise result. The sodium consumed is sufficiently near the theoretical quantity. The oil is of necessity below the mark: at least ·5 grm. would be lost by adhesion to the dish in which it was heated to drive off ether; there is a source of loss by evaporation and by solution in the water used to wash it.

On comparing the composition of the oil with the composition of valerianic ether,

| | Valerianic ether. | Valeryl. | Found. |
|---|---|---|---|
| C | 64·62 | 70·59 | 71·48 |
| H | 10·77 | 10·59 | 11·67 |
| O | 24·61 | 18·82 | 16·85 |
| | 100·00 | 100·00 | 100·00 |

it is manifest that the oil cannot be unattacked valerianic ether; it is therefore certain that the sodium which had disappeared had used up the valerianic ether taken for the experiment.

The oil approximates in composition to valeryl, the slight excess of carbon and hydrogen being probably due to the presence of a little hydrocarbon—the product of a slight secondary action of sodium upon valeryl. The circumstance that the sodium consumed is slightly in excess over the sodium found caustic, is quite in accordance with there having been a slight degree of secondary action on the valeryl.

In another experiment an oil was obtained which gave on analysis:—

| | |
|---|---|
| Carbon ...... | 71·52 |
| Hydrogen ...... | 11·04 |
| Oxygen ...... | 17·44 |
| | 100·00 |

Freund* has shown that an amalgam of one part of sodium and two parts of mercury liberates a compound having the composition of butyryl from chloride of butyryl. It boils between 245° and 260°C. and appears to suffer decomposition on distillation.

Valeryl should be more readily decomposed than butyryl. I was therefore indisposed to attempt a purification of my product by means of distillation. It will be far easier so to modify the original reaction as to obtain it pure in the first instance. With this part of the investigation I am at present engaged. Meanwhile the fact that one molecule of valerianic ether is completely decomposed by one atom of sodium, and that the one atom of sodium appears in the caustic state, whilst the resulting oil has very nearly the composition of valeryl, is conclusive evidence that the reaction between sodium and valerianic ether is correctly represented by the equation

$$2 \cdot \left.\begin{matrix} C_5H_9O \\ C_2H_5 \end{matrix}\right\} O + Na_2 = 2 \cdot \left.\begin{matrix} Na \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} C_5H_9O \\ C_5H_9O \end{matrix}\right\}$$

---

* Ann. Ch Pharm., cxviii, 33.

With potassium the reaction is the same. One equivalent of potassium dissolves in one molecule of valerianic ether, and is subsequently found in the caustic state, whilst an oil separates just as before. In making the experiment with potassium the greatest caution is required: with care, the reaction may be effected with the greatest precision; without proper attention an explosion is the result.

From the great interest belonging to the acid-forming radicles it is my intention to prepare large quantities of valeryl, and to make a minute examination of its chemical character.

The principal other acid-forming radicles, including benzoyl, will be also sought by a similar procedure.

## XLIV.—*On the Occurrence of Nickel in Lead, and its Concentration by Pattinson's Process.*

By Wm. Baker, Associate of the Royal School of Mines.

It is well known that, for certain manufactures, lead of a high degree of purity is required. The presence of a very small amount of copper is especially injurious for making white lead and glassmakers' red lead. Investigating the cause of a peculiar tint in glass, which was sometimes sufficiently marked to be called blue, and was readily accounted for by the presence of copper, I sought carefully for cobalt, but only found nickel. In all the samples of English lead which I have examined I have never detected a trace of cobalt. On the contrary, traces of nickel have frequently been found in various samples of Derbyshire lead, in Yorkshire lead, and lead from Snailbeach. Operating upon 2000 grains, I have found the following quantities of nickel in the pig lead as delivered by the smelter:—

| | | | oz. | dwts. | gr. | |
|---|---|---|---|---|---|---|
| Derbyshire lead, 1st sample.... | 0·0023 % | = | 0 | 14 | 8 | per ton. |
| Do. 2nd ,, .... | 0·0031 ,, | = | 0 | 19 | 14 | ,, |
| Do. 3rd ,, .... | 0·0023 ,, | = | 0 | 14 | 8 | ,, |
| Snailbeach lead.............. | 0·0007 ,, | = | 0 | 5 | 10 | ,, |
| Softened slag lead............ | 0·0057 ,, | = | 1 | 16 | 14 | ,, |

On submitting lead containing these quantities of nickel to Pattinson's process, I find a concentration of the nickel in the fluid portion. Crystals of lead were taken out in the proportion of $\frac{9}{10}$, leaving $\frac{1}{10}$ fluid lead of a 5-ton charge.

Samples of the fluid lead or "bottoms," upon analysis, contained nickel as follows:—

| | | | oz. | dwts. | gr. | |
|---|---|---|---|---|---|---|
| After 3 | crystallisations | 0·0047 = | 1 | 10 | 1 | per ton. |
| After 1 | do. | 0·0043 = | 1 | 7 | 10 | ,, |
| After 1 | do. | 0·0062 = | 2 | 0 | 12 | ,, |
| After 2 | do. | 0·0072 = | 2 | 7 | 0 | ,, |

In all cases a weighable quantity could be obtained from 2000 grains of lead.

Five tons of lead contained ·0068 % = 2 oz. 4 dwts. 10 gr. per ton. Four and a half tons were removed as crystals, and when melted contained only ·0047 % = 1 oz. 10 dwts. 1 gr. per ton. These figures show that nickel remains to a great extent with the fluid portion, much as copper does; and I have reason to suppose that when it reaches a certain amount, as is the case with copper, the separation is no longer effected, or only in a very small degree. In the case of copper this is easily understood, when it is seen that, at a low temperature, copper (in the absence of antimony and arsenic) will separate and be found in the dross on skimming, leaving the fluid lead, containing about 20 oz. per ton = 0·06 %. To effect a separation of the copper by Pattinson's process, the amount at the commencement should not be more than 10 oz. per ton.

A sample of lead from 5 tons, when analysed, gave no indications of the presence of nickel; on crystallizing $\frac{9}{10}$, the remainder gave distinct traces of the metal. In refined lead, I have only once succeeded in obtaining a weighable quantity, and only rarely found traces of nickel. That it is not removed by oxidation is proved by the larger quantity found in the fluid portion of the lead when crystallized, as well as by the fact that in the softened slag lead which is submitted to the powerful oxidizing action of nitrate of soda, a considerable quantity of nickel is still found.

# XLV.—*On the Colouring Matter of Blue Forest Marble.*

By A. H. Church, M.A., Oxon., Professor of Chemistry, Royal Agricultural College, Cirencester.

The existence of dark bands or zones in that member of the Great Oolite series known as the Forest Marble, has been frequently noticed by geological observers. My attention was directed to the subject by Professor John Morris, and at his suggestion, determinations of the total amount of sulphur in the dark and the light parts of a fragment of the banded forest marble were made in my laboratory by Mr. C. C. Jacobsen. He found that the dark band gave, after fusion with nitre and carbonate of sodium, just twice as much sulphate of barium as the lighter exterior of the stone.

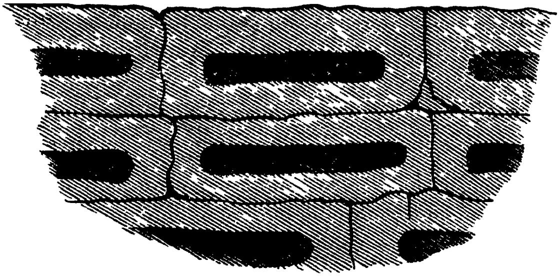
| | | | | |
|---|---|---|---|---|
| The dark stone | contained | ·50 | per cent. | of sulphur. |
| ,, light ,, | ,, | ·24 | ,, | ,, |

The result induced me to pursue the subject further, and with the able assistance of Mr. R. Warington, junior, I have at last arrived at a satisfactory conclusion as to the true nature of the grey (or bluish grey) colouring matter of the forest marble. The investigation has proved tedious, and the results may not seem commensurate with the labour expended, yet it is probable that, upon minute and apparently insignificant peculiarities of composition, such as those I shall presently point out, may depend very important geological changes.

A few words of preface are requisite, in order to show the mode in which the dark band occurs.

On examining a section of the Forest Marble, it will be found that the dark bands invariably occupy the central portion of the various sized slabs into which the stone has naturally divided, that is to say, the dark band is not horizontally continuous, but is broken by each vertical fissure of the rock, as shown in the accompanying diagram.

Even when there is considerable dip in the stratum, the dark band still occupies its place in the centre of each slab of stone. The dark band frequently constitutes nine-tenths of the bulk of a thick slab, if it be of compact texture. Very thin slabs sometimes are without a dark band. The dark stone is more abundant, and becomes of a deeper tint as we descend. The lowest layers rest upon a stratum of blue clay of exactly the same tint as the dark



stone, and owing its colour to the same substance. In one section which I have examined, where many of the slabs had a thickness of three inches, the light buff tint was seen to surround the dark grey band on all sides to the depth of about one inch. The exterior of the slab is stained russet-brown with ferric oxide.

The boundary between the dark and light (or grey and yellow) parts is perfectly well defined. There is no shading of one tint into the other. The colour of each part is also very uniform, not only in the same fragment, but in specimens from distant quarries. Occasionally, however, shells and small pieces of lignite occur irregularly scattered throughout the stone.

I may now proceed to describe as succinctly as possible the various experiments qualitative and quantitative which have been made with the view of comparing the dark and light stone. Firstly, as to the experiments with the

## DARK STONE.

When the finely powdered dark stone is dissolved in hydrochloric acid, and the whole of the evolved gases passed through acetate of lead solution, no blackening occurs.

The existence of iron in the condition of a ferrous compound was proved by ferricyanide of potassium, the hydrochloric solution of the dark stone giving a blue precipitate with that reagent. Permanganate of potassium was also decolorised by it.

On ignition to full redness in a closed glass tube, no tarry matter distilled, and the dark grey colour of the stone remained unchanged. The small quantity of water condensed in the tube was found to have an acid reaction, and to contain sulphuric acid.

The dark stone heated to redness, with free access of air, assumed a pale reddish tint.

### LIGHT STONE.

This variety of forest marble was found to contain iron in two conditions, and also sulphur, oxidized and unoxidized.

### DARK STONE.

After these experiments, attention was more especially directed to the iron and sulphur present in the materials under investigation. The first step was to ascertain whether any of the sulphur known to be present (in some form or other of combination) in the dark stone could be removed by the action of water. For this purpose, the finely powdered dark stone was boiled for five hours with ten ounces of water, and the filtrate acidified and precipitated with BaCl.

I. 150 grains *dark* stone gave ·59 grains $Ba_2SO_4$ = ·162 p. c. $SO_4$.

### LIGHT STONE.

The light stone was similarly treated, with the following result:

II. 150 grains *light* stone gave ·07 grain $Ba_2SO_4$ = ·019 p. c. $SO_4$.

The percentage of $SO_4$ thus obtained from the light stone is but one-eighth of that which can be extracted by the same process from the dark stone. This result is explicable if we admit that the outside or light portion of the stone has been already submitted naturally to the action of water, which has not penetrated so as to affect the dark interior.

### DARK STONE.

The action of hydrochloric acid upon the dark stone was next studied,—the amount of sulphuric acid as well as of ferrosum* and ferricum extracted by that reagent being determined.

III. 66·3 grains gave ·35 grains $Ba_2SO_4$ = ·217 p. c. $SO_4$.

IV. 50·9 grains gave by permang. process (*ferrosum*) = ·313 p. c. Fe.

---

* I here include under this expression, iron, whether existing in ferrous compounds proper, or in combination with sulphur, &c., as in pyrites.

V. 50·06 grains gave by permang. process (*ferricum*) = ·043 p. c. Fe.

VI. 50·06 grains gave by permang. process (*total iron*) = ·356 p. c. Fe.

VII. 66·3 grains gave by permang. process (*total iron*) = ·336 p.c. Fe.

It is especially to be noted here that scarcely more than one-seventh of the iron extracted by hydrochloric acid from the dark stone exists as ferric compounds. This result is in striking contrast with the annexed experiments.

### LIGHT STONE.

Similar analyses to those just given were made in the hydrochloric acid solution of the light stone.

VIII. 76·05 grains gave ·21 grains $Ba_2SO_4$ = ·122 p. c. $SO_4$.

IX. 51·94 grains gave by permang. process (*ferrosum*) = ·209 p. c. Fe.

X. 51·94 grains gave by permang. process (*ferricum*) = ·201 p. c. Fe.

XI. 51·94 grains gave by permang. process (*total iron*) = ·410 p. c. Fe.

### DARK STONE.

After treatment of the powdered dark stone with tolerably strong hydrochloric acid, till no further action took place, boiling with water, and washing the residue till the filtrate was free from calcium-salts, the whole of the dark colouring matter appeared to remain unaltered. It was separated from the main bulk of the sand by careful decantation, and submitted to analysis in order to determine the sulphur and iron present in it.

XII. 69·6 grains of dark stone gave 1·86 grains $Ba_2SO_4$.

When from this *total* amount converted into a per centage (2·672), the per centage of $Ba_2SO_4$ (·527), yielded by the portion of the dark stone soluble in hydrochloric acid, is deducted (thus: 2·672 — ·527 = 2·145), we may arrive at the per centage of sulphur in the part of the dark stone insoluble in acid:

2·145 p. c. $Ba_2SO_4$ = ·294 p. c. sulphur.

XIII. 66·3 grains gave, by permanganate process (in the insoluble part) ·231 p. c. iron.

### LIGHT STONE.

The action of hydrochloric acid upon the light stone, by removing the greater part of the iron existing in it as ferric oxide, caused its buff colour to disappear, a residue remaining which partook, to a modified extent, of the physical and chemical properties of the residue similarly prepared from the dark stone.

XIV. 68·92 grains (the insol. matter from) gave ·93 grm. $Ba_2SO_4$ = ·133 p.c. sulphur.

XV. 68·92 grains (as above), by permang. process, gave ·079 p. c. iron.

The bearings of the various experiments already recorded may be best seen by an examination of the results in a tabulated form:

Percentage of *Iron* and *Sulphur* in the *Dark* and *Light* bands of Forest Marble.

| | | Dark. | Light. |
|---|---|---|---|
| Soluble in Water | $SO_4$ | ·162 | ·019 |
| Soluble in hydrochloric acid | $SO_4$ | ·181 | ·102 |
| „ „ „ | Ferrosum | ·318 | ·209 |
| „ „ „ | Ferricum | 031 | 201 |
| „ „ „ | Total Iron | ·346 | ·410 |
| Insoluble in hydrochloric acid | Sulphur | ·294 | ·133 |
| „ „ „ | Iron | ·231 | ·079 |
| Total Soluble and Insoluble | Sulphur | ·366 | ·171 |
| „ „ „ „ | Iron | ·583 | ·489 |

To sum up the chief conclusions at which we may arrive from the results of the experiments hitherto given:—

1. The sulphur in the soluble part of the dark stone most probably exists as sulphates, since it is extracted by water as well as by hydrochloric acid.

2. The sulphur in the insoluble part probably exists in the form of a sulphide, insoluble in acids, for it has to be oxidized before a precipitate is obtained with barium salts.

3. From the fact that in the dark stone by far the larger part of the iron exists in an unoxidised condition, and that much of this iron remains in that part of the dark stone which is insoluble in hydrochloric acid, it is probable that it is, in part at least, there combined with sulphur as the insoluble sulphide, pyrites, $Fe_2S_2$.

### DARK STONE.

In order to verify, if possible, the above hypothesis, attempts were made to effect a further purification of the dark matter insoluble in hydrochloric acid. For this purpose the dark insoluble matter was separated mechanically from the accompanying grains of sand. This was effected by adding water, agitating and decanting the turbid liquid before the finely-divided dark particles had had time to subside. In this way the grey colouring material of the stone was obtained in a more concentrated form. It was further purified by a second treatment with hydrochloric acid and washing.

After drying at 100°, the prepared dark matter, when ignited with access of air, became bright red, evidently owing to the oxidation of the iron compound present.

Ignited in a small tube closed at one end, it gave off water and a considerable quantity of hydrosulphuric acid. A very distinct sublimate of sulphur was formed: the residue was now quite black, and when treated with hydrochloric acid gave off sulphuretted hydrogen abundantly, though the original dark substance had been prepared by treatment with hydrochloric acid. This behaviour quite accords with that of pyrites, which is unaffected by hydrochloric acid until it has been ignited, when the residual magnetic sulphide is easily decomposed by acids.

After fusion with pure nitre, the dark grey matter became bright red: the mass boiled in water gave a solution in which abundance of sulphate of potassium was found.

Boiled with strong hydrochloric acid, the dark matter suffers no change; the addition of a drop of nitric acid at once causes the grey colour to disappear.

The dark matter was found to be quite free from uncombined sulphur.

The insoluble matter from the dark stone contained a few particles of mica and some fragments of lignite.

Determinations of iron and sulphur in the prepared dark substance were made, with the following results:—

XVI. 4·89 grains dark substance, dried at 100° C, gave after fusion with carbonate and nitrate of potassium 3·07 grns. $Ba_2SO_4$ = 8·63 p. c. sulphur.

XVII. 4·89 grns. dark substance, dried at 100°, gave after fusion with carbonate and nitrate of potassium by permang. process = 8·272 p. c. iron.

If foreign matters be deducted, these numbers correspond to the following per centage proportions of sulphur and iron:—

| | The prepared dark matter. | Sulphide of iron $Fe_2S_2$. |
|---|---|---|
| Sulphur ...... | 51·05 | 53·34 |
| Iron ........ | 48·95 | 46·66 |
| | 100·00 | 100·00 |

These results, taken in connection with the qualitative experiments, leave no doubt that the dark stone owes its colour to sulphide of iron—common pyrites.

### Light Stone.

The behaviour of the dark matter prepared from the light stone is similar to that of the dark stone, but from its containing but little pyrites that has escaped oxidation, its colour is much weaker; and in the light stone itself, this grey colour is completely masked by the ferric oxide there present.

There is a slight difference in specific gravity between the dark and light varieties of the forest marble. Specimens were taken from three quarries, and the dark and light parts having been separated in each case, the following numbers were obtained:—

| | | | | Difference. |
|---|---|---|---|---|
| I. | Dark band | Specific gravity | 2·627 | ·036 |
| | Light " | " " | 2·591 | |
| II. | Dark " | " " | 2·631 | ·031 |
| | Light " | " " | 2·600 | |
| III. | Dark " | " " | 2·585 | ·023 |
| | Light " | " " | 2·562 | |

It will thus be seen that the dark part of any given specimen was of greater density than the light part. If we may assume that the stone was once wholly of the dark kind (and this assumption is supported by the occurrence throughout the stone of lignite rich in pyrites), this alteration of density becomes of some interest, for to the expansion probably consequent upon this alteration some of the physical appearances of the beds of stone may be due. On the other hand, it is possible that the oxidation and consequent gain in weight of the oxidizable iron pyrites, &c., of the stones, may have been more than counterbalanced by the loss arising from the solvent action of water upon one of the products of this oxidation, namely, the sulphate of calcium, which, as one of my experiments shows, is contained in comparatively most minute proportion in the light stone.

I think, from the foregoing experiments, I am completely justified in concluding iron pyrites to be the colouring material of the dark bands of the forest marble; and that the paler yellow, brown, or buff tint of the outer parts of the slab of this stone is due to the ferric oxide resulting from the oxidation of the pyrites. Fine sand ground up with no more than one per cent. of pyrites present very much the appearance of the dark stone; while the separated dark substance, containing 16 p. c. $Fe_2S_3$, may be exactly imitated by a similar artificial mixture of sand and pyrites.

As will have been noticed (ante) the blue clay underlying the forest marble is, sometimes at all events, similarly coloured with pyrites; and it is probable that the same explanation of the phenomenon under discussion may be extended to other blue and grey-coloured clays, rocks, soils, &c.; in fact, iron pyrites appear to have been detected before in somewhat similar circumstances; and close to a stratum containing this mineral in abundance, Bischof found (at Röndorf) a chalybeate spring rich in ferrous carbonate, and also containing sulphates.

In an agronomic point of view, the facts I have related would appear of some importance, since we may now be able to trace the cause of the injurious influence which these blue and grey matters exert on vegetation.

## XLVI.—*Some Experiments on the Density of Garnet, Idocrase, &c.*

By A. H. Church, M.A., Professor of Chemistry, Royal Agricultural College.

It has recently been stated* that the garnets and the members of the idocrase group, if heated to redness without fusion, diminish considerably in density. I was engaged upon some experiments on a kindred subject, when I met with this statement; and having all the necessary materials and apparatus at hand, I determined to examine for myself the phenomenon in question. In the present note I give some of the results which I have obtained with specimens of idocrase and garnet, appending a few observations as to the effect of heat on three or four minerals of different types.

---

* Proc Roy. Soc., vol. xiii, p. 241.

*Idocrase.*—A large crystal of Vesuvian idocrase, of a dark olive tint verging on brown, was selected for experiment. Its density was determined; it was then maintained at a bright red heat for 15 minutes, and, after cooling, its density was again ascertained. Finally, it was heated for 17 minutes to incipient fusion in a Herapath's gas blow-pipe urged by bellows, each face of the crystal being exposed in succession to the hottest part of the flame. The heat had to be moderated, for slight intumescence and fusion began to be apparent. Its density was determined for the third time, after this prolonged ignition; the following are the results:—

| | Weight. | Density. |
|---|---|---|
| Before heating .. .. .. .. | 6·9855 grm. | 3·3838 |
| After having been heated to redness without trace of fusion for 15′ .. | 6·9855 grm. | 3·3838 |
| After having been heated to incipient fusion for 17′ .. .. .. .. | 6·9835 grm. | 3·3843 |

A second experiment was made, this time with green idocrase, from Ala in Piedmont. The mineral was heated exactly as already described, in the first instance to a bright red heat, in the second to incipient fusion; the following are the results:—

| | Weight. | Density. |
|---|---|---|
| Before heating .. .. .. .. | 2·9472 grm. | 3·4 |
| After having been heated to redness without trace of fusion for 15′ .. | 2·9470 grm. | 3·401 |
| After having been heated to incipient fusion for 15′ .. .. .. .. | 2·9470 grm. | 3·401 |

Several portions of the specimens were now broken off, and fused completely in loops of platinum wire; the density of many such idocrase beads was determined, in some cases four beads being weighed together. The mean of three accordant experiments gives 2·937 as the density of fused idocrase. These experiments further confirm the original statement of Magnus, that idocrase, when fused, has a lower density than the crystallized mineral, while they also shew that mere heating to redness without fusion, or even with traces of fusion, does not reduce the density of idocrase.

*Garnet.*—The experiments performed with idocrase were repeated with several varieties of garnet, and generally with similar results. I will first show the effect of heat on well crystallised specimens of brownish red iron-garnet from Arendal:—

| | Density. | | | |
|---|---|---|---|---|
| | I. | I. | III. | IV. |
| Before heating.. .. .. | 4·058 | 4·059 | 4·059 | 4·059 |
| After heating to incipient fusion for 15′ .. .. .. | 4·045 | 4·059 | — | — |
| After complete fusion to a bead | 3·596 | 3·401 | 3·395 | 3·204 |

Thus we see that heating iron-garnet to full redness for a quarter of an hour, does not affect its density, while actual fusion lowers it remarkably, in one instance from 4·059 to 3·204. Another experiment, in which an (almandine) iron-garnet was employed gave a different result. Though prolonged ignition had no effect in changing the density of the specimen, when it was almost completely fused, its density had risen from 4·103 to 4·208.

In the case of lime-garnet two varieties were examined I and II were essonite from Ceylon; III was topazolite.

| | Density | | |
|---|---|---|---|
| | I. | II. | III. |
| Before heating .. .. .. | 3·604 | 3·666 | 3·613 |
| After ignition to full redness for 15′ | 3·605 | 3 666 | — |
| After ignition to incipient fusion .. | — | 3·682 | 3·7 |

Here it may be noticed that long-continued ignition has merely produced a slight increase in the density of the specimens of lime-garnet submitted to experiment.

*Olivine, &c.*—I have further examined the effect of a strong red heat continued for 15 minutes on many well crystallised transparent minerals. Some of the results where the density remained unaltered, or was slightly reduced, are given in the annexed list:—

| Name of mineral. | Density before ignition. | Density after ignition. |
|---|---|---|
| *Olivine.* — Pistachio green, the variety peridot; became greenish-brown when hot, original colour when cold .. | 3·389 | 3·378 |
| *Beryl.* — Straw-yellow, became (permanently) blue on ignition .. .. | 2·697 | 2·697 |
| *Chrysoberyl.*—Golden-yellow . .. | 3·84 | 3·833 |
| *Topaz.*—Sherry-yellow; became colourless on ignition, and permanently pink on cooling . .. .. . | 3·539 | 3·533 |

*Zircon.*—The density of zircon is known to be increased by heating, and this increase would seem to be permanent. M. Damour has recently examined the question. The range of density in the specimens he worked with was between 4·04 and 4·67. One Ceylon zircon had the density 4·183, but M. Damour found that after it had been heated to redness, its density had increased to 4·534. Most of the specimens used as gems come from India and Ceylon, and present a high density; in fact, they have been heated in order to enhance their value as jewels: for heating is attended with increase of brilliancy and transparency, and more or less complete loss of colour. I have twice taken the density of a large yellow-brown Indian-cut zircon in my possession, weighing 2·198 grammes—the interval between the determinations having been more than six months. The density was 4·696 on both occasions. It showed no sign of returning to the lower density of native zircon.

A pale olive-green zircon was next examined. It was Indian cut, without a flaw, very brilliant, and transparent. It weighed 1·1665 grammes. Its density was found to be 4·579. It was heated for five minutes to low redness, and its density again ascertained; it remained unaltered. The stone was now submitted to a still higher temperature, the highest attainable by means of a large Herapath's blow-pipe urged by bellows. After the specimen had cooled, its density was again ascertained. It was now found to be rather greater, namely, 4·625. The colour of the stone had become somewhat reduced.

In all the determinations of density recorded in the present communication, every precaution was taken to ensure the greatest accuracy in the results. Every mineral used was identified with certainty with the species to which it is here referred.

# XLVII.—*On the Existence of Nitrogen in Steel.*

By Graham Stuart, F.G.S., F.C.S., and Wm. Baker, F.C.S.,
Associate of the Royal School of Mines.

The experiments which we are about to lay before the Society were undertaken with the intention of throwing some further light upon the vexed question, "Is nitrogen an essential constituent of steel;" and if so, of showing whether its presence in greater or less quantity could be held to account for the difference in quality of various kinds of steel.

In pursuance of these objects, we have repeated Frémy's experiments for the purpose of estimating the amount of nitrogen contained in different samples of both steel and iron, including *cast steel, blister steel,* and iron of the well known mark , *Bessemer steel, specular iron* (*Spiegeleisen*), a kind of iron now used to a considerable extent for further carburizing steel during the ordinary process of refining, wrought iron of English manufacture, and the same converted into steel at a full red heat in a current of carbonic oxide.

The apparatus used in these experiments has been varied considerably during their progress, but the general plan of investigation has remained the same throughout, and the alterations have only been intended to secure more completely those conditions which were found to be absolutely indispensable to obtaining a correct result. Those conditions may be briefly stated as consisting either in the total exclusion of nitrogen, in whatever shape or form, from the apparatus and the gas used, or, as we found in some cases more satisfactory, in the employment of such a modification of the apparatus as would admit of our estimating what quantity of the nitrogen obtained was due to any sources other than the steel under examination.

The general method of experimenting was as follows—Hydrogen, purified, and more or less dried, was passed over the steel or other substance under analysis heated to full redness, and was then conducted into a Wills' nitrogen apparatus, where the ammonia generated by its passage over the red-hot steel, was absorbed in a standard solution of sulphuric acid, and its amount afterwards estimated by volumetric analysis. It was then of course easy to calculate the quantity of nitrogen contained in the steel.

In the first experiments, no means were taken specially to exclude or make allowance for the nitrogen that might be present as air, either mixed with the hydrogen in the gasometer, or in the tubes of the apparatus before the commencement of the experiment, reliance being placed in the former case upon the hydrogen being prepared with such care as to insure its purity, and in the latter, upon the gas being passed through the apparatus a sufficiently long time to sweep out the air previously contained in it before the experiment was commenced.

The above remarks apply more particularly to experiments No. 1 to 11 inclusive, in which the apparatus used consisted merely of—

1. Solution of potash.
2. Column of pumice wetted with sulphuric acid.
3. A U drying tube of chloride of calcium.
4. The analysis tube.
5. Will's nitrogen bulbs filled with standard acid.

The steel in all the experiments was used in the form of fine powder (passed through a muslin sieve), filings, grains (the size of ordinary shot) or strips, about 3 inches to 4 inches long, $\frac{1}{4}$ inch to $\frac{1}{8}$ inch wide, and about $\frac{1}{50}$ inch to $\frac{1}{100}$ inch in thickness. The passage of the gas through the potash-bulbs varied from the rate of 50 to 150 bubbles per minute, and was continued after the heat was withdrawn until the assay tube was cool. The following Table (No. 1) exhibits the result of the first eleven experiments just mentioned; by a reference to it, it will be noticed that in all these instances, except in No. 2, nitrogen was obtained, though varying in quantity, from ·007 % to ·068 %.

TABLE I.

| No of Expt. | Description and state of steel employed. | Quantity of steel. | Duration of Expt. | Amount of N. obtained. |
|---|---|---|---|---|
| 1 | β Blister steel, in grains.. | 50·000 grm | 1 hour | ·068 per cent. |
| 2 | ,, ,, | 25 000 ,, | 2 ,, | ·000 ,, |
| 3 | ,, ,, | 25·000 ,, | 2 ,, | ·0293 ,, |
| 6 | ,, ,, | 33·3345 ,, | 2½ ,, | ·020 ,, |
| 7 | Cast steel, in strips.......... | 37 93075 ,, | 1½ ,, | ·027 ,, |
| 8 | ,, ,, | 18·6415 ,, | 3½ ,, | ·018 ,, |
| 9 | Bessemer steel, in filings...... | 50 000 ,, | 2 ,, | 011 ,, |
| 11 | ,, ,, | 55·723 ,, | 1½ ,, | ·007 ,, |

These experiments we consider as preliminary ones only, and judging from the experience we afterwards obtained, must reject altogether Nos. 1, 3, 6, and 7 as being incorrect, from the nitrogen obtained being, at all events in part, derived from other sources than the steel; most probably from some air remaining in the apparatus when the experiment was commenced; and when the comparatively large quantities of nitrogen obtained are taken into account, there can remain but little doubt that this source of error vitiated the results in all these instances.

Experiment No. 2 demands a special notice; it seems to have given what we must now look upon as an accurate result; however, as it was only the second experiment of the kind that we had made, we do not feel justified in laying any very great stress upon it, although, in referring to our note-book, we do not find any further reason to doubt its accuracy. In experiments Nos. 8, 9, and 11 the amount of nitrogen found has materially decreased. This may probably have arisen from the precautions requisite to insure an accurate result becoming better understood, and especially to extra care being taken in preparing the hydrogen, and in driving out the air from the apparatus more completely before commencing the experiments. We therefore consider these three entitled to more confidence than the preceding ones.

On comparing all these experiments generally together, however, a gradual but unmistakeable decrease in the amount of nitrogen was at once apparent. This appeared strange, and aroused a suspicion that possibly much, if not all of it, might be due to other sources than the substance under examination, and it was evident that more careful experiments were necessary to arrive at a perfectly correct result. It was therefore determined to try if the nitrogen present in the apparatus could not be entirely removed, so as to insure the hydrogen arriving at the assay-tube in a state of absolute freedom from this impurity. The best method of doing this seemed to be to convert it into ammonia, and to absorb it in this state by dilute acid; and the apparatus was accordingly modified thus :—

1. Flask containing potash as before.
2. Tube filled with soda-lime, at a red heat, and about six inches in length.
3. Dilute sulphuric acid.
4. Assay-tube.
5. Wills' nitrogen bulbs filled with standard acid.

The distance between the sulphuric acid and the steel was made as short as possible, with the view of reducing to a minimum the quantity of air it would contain, and the further precaution was taken of passing the gas over the soda-lime for some time before the steel was heated. It will thus be seen that if any nitrogen was present, either in the hydrogen, or in the apparatus it would become converted into ammonia by passing over the soda-lime, which passing onwards would be absorbed by the sulphuric acid. There would now remain only the small space above the liquid in the sulphuric acid bottle, and the short and narrow tube between it and the assay-tube in which any air could lodge to vitiate the results.

With this arrangement, experiments 13 to 17 were made, Nos. 13 and 14 were made upon cast steel, in thin strips similar to those previously described, and Nos. 15 and 17 upon *specular iron* crushed to powder in a steel mortar and passed through a fine muslin sieve. It will be noticed by a reference to Table No. 2 that considerable quantities of these substances were used, but in only one case was any nitrogen detected. This was in No. 15, upon specular iron, but there seems to be some doubt respecting the accuracy of this experiment, for from a remark in our note-book it seems that the assay-tube was heated before the air was entirely expelled from it, and as in the subsequent experiments upon the same substance none gave any nitrogen whatever, it is probable that this or some other error must have crept in.

TABLE II.

| No. of Expt. | Kind and state of substance employed. | Quantity used. | Duration of Expt. | Amount of N. obtained. |
|---|---|---|---|---|
| 13 | Cast steel in strips ............ | 27·081 grm. | 1 hour. | ·000 per cent. |
| 14 | ” ” | 26·706 ” | (?) | 000 ” |
| 15 | Specular iron, in fine powder.... | 20·583 ” | 3 hours | ·015 ” |
| 17 | ” ” | 20·000 ” | 1 ” | ·000 ” |

In all these experiments the gas issuing from the soda-lime tube was tested for ammonia by placing small pieces of reddened litmus-paper in the narrow tube leading from it into the sulphuric acid bottle. They invariably gave indications of its presence, and traces of it could be found even after the hydrogen had been passing through for more than an hour.. The assay-tube was never heated until these traces had entirely disappeared.

In the next series of experiments that were made, the soda-lime tube was dispensed with, and no means were taken to absorb the nitrogen in the apparatus. The hydrogen was prepared with every possible precaution however, and was passed direct from the gas-holder into the assay-tube, without any intervening apparatus, except a wash-bottle filled as full as practicable with a solution of protosulphate of iron, made slightly alkaline with potash. As short an apparatus as possible was used, and the hydrogen passed through it for a long time before heat was applied to the assay-tube, the object being to reduce the amount of air contained in the apparatus to the least possible quantity, and to sweep it out completely, so as to prevent the nitrogen it contained from interfering with the result. The protosulphate of iron was intended to absorb any oxygen that might be present, it being frequently found that the steel was slightly oxidised when the experiment was ended. It was replaced for experiments Nos. 51 and 52 by a solution of oxide of lead in potash. This was used to absorb hydrosulphuric acid, a small quantity of which was given off during some of the experiments.

This method was found to answer very well in practice, although of course open to the objections which have been stated before; very great care is however requisite in making the experiments, but when sufficient attention is given to them, it may be relied upon for giving correct results.

In Table No. 3 a detailed account of the experiments made with this arrangement is given. A glance at it will show that in the whole series we obtained no amount of nitrogen that could be considered of any importance, even with the possible chance of the errors we have previously pointed out, and we therefore submit that the negative results obtained in these instances are very strong evidence that nitrogen is not an essential constituent of steel.

TABLE III.

| No. of Expt. | Kind and state of steel employed. | Quantity used. | Duration of Expt. | Amount of N. obtained |
|---|---|---|---|---|
| 19 | Specular iron in fine powder .. | 7·190 grm. | 0¾ hours. | ·000 per cent. |
| 20 | Cast steel in strips .......... | 15·536 „ | 3¼ „ | ·000 „ |
| 21 | Iron in strips .............. | 25·713 „ | 2 „ | ·0051 „ |
| 23 | Cast steel in filings .......... | 14·6215 „ | 6 „ | ·000 „ |
| 24 | „ „ | 15·077 „ | 3 „ | ·000 „ |
| 35 | „ „ | 40·057 „ | 3 „ | ·0023 „ |
| 51 | Steel made by heating iron in C.O.................... | 8·005 „ | 2 „ | ·0015 „ |
| 52 | Spiegeleisen in grains........ | 80·000 „ | 4 „ | ·000 „ |

In three of the above experiments slight traces of nitrogen were discovered. Still the amounts are so very small that they cannot be looked upon as essential to the constitution of steel, especially when so many other experiments fail to show any trace whatever of nitrogen.

In the succeeding experiments, an important alteration was made in the apparatus, which requires a short description. Two tubes, one containing the steel to be operated upon mixed with soda-lime, and the other containing soda-lime only, were placed side by side in the same furnace, and heated to the same temperature, whilst the hydrogen was passed from the same gas-holder through both, the current being so regulated that an equal quantity passed through each tube in a given time. Previously to its entering the tubes, the hydrogen was washed by passing successively through a solution of hydrate of potassium and dilute sulphuric acid, and in some cases was partially dried by passing through concentrated sulphuric acid immediately before its entrance into the steel and soda-lime tubes. The first of these was made upon cast-steel filings, 6·355 grm. of which were taken and intimately mixed with 6·3 grm. of soda-lime, 6·3 grm. of soda-lime alone being placed in the second tube. Both were heated to a full red heat for 2½ hours. No nitrogen was obtained. The whole of the series were made in a precisely similar manner, Nos. 25, 30, and 36 upon cast steel in filings, and Nos. 32, 33, 34, and 37 upon ℬ, blister steel and iron of the same mark, also in filings. A reference to the following Table will show the results obtained :—

Table IV.

| No. of Expt. | Quantity of steel employed. | Kind and state of steel employed. | Quantity of soda-lime mixed with the steel. | Duration of expt. | Amount of N. obtained. |
|---|---|---|---|---|---|
| 25 | 6 355 | Cast steel in filings ........ | 6 ·3 | 2½ hrs. | ·000 per cent. |
| 30 | 5 ·000 | „ „ | 5 ·0 | 6½ „ | ·000 „ |
| 32 | 5 091 | ℬ Blister steel in filings .. | 5 ·0 | 4½ „ | ·000 „ |
| 33 | 10 117 | „ Iron „ „ | 5 ·0 | 3 „ | ·000 „ |
| 34 | 9 ·980 | „ Blister steel „ | 5 3 | 2 „ | ·010 „ |
| 36 | 21 ·0405 | Cast steel in filings ........ | 15 ·0 | 2 „ | 0009 „ |
| 37 | 19 ·456 | ℬ Blister steel in filings .. | 6 ·7 | 1 „ | ·0040 „ |

There is one remark to be made respecting the length of time that the steel was submitted to the action of hydrogen in these experiments. It was invariably found that the greater part of the nitrogen, in those cases where any was obtained, was given off in the earlier part of the time, and that, in the latter part, no indication could be found. It appears very probable from this that in those instances the nitrogen was supplied by the air in the apparatus.

In judging of these experiments, it must also be borne in mind that if any of the samples of steel operated upon had contained nitrogen, the method of analysis could not have failed to show it, and therefore it cannot be said that it may have been present in cases where we have failed to detect it; whilst it is equally certain that any that might have been accidentally present in the apparatus would have been shown. Thus, in cases where nitrogen was obtained, every allowance for error must be made; whilst in those in which absolutely none could be detected, the results must be rigidly adhered to.

Having now given a full description of the methods of experimenting, we would next direct attention more particularly to the different kinds of steel and iron employed, and the quantity of nitrogen obtained from each.

Excluding, for the reasons previously given, the first five experiments, there are four made upon B blister steel, and iron. Of these two, Nos. 32 and 33, gave absolutely no nitrogen, whilst the others, Nos. 34 and 37, gave only ·004% and ·010%, quantities which, in our opinion, were due to the sources of error before-mentioned. Taking the average, ·0036% is obtained, an amount which is too small to be considered of any moment. These were all made upon the same sample in the state of filings.

Next follow ten experiments upon cast steel. These were made partly on cast steel in the form of strips, and partly as filings. In these a remarkable unanimity is observable in the results, for out of the ten, eight gave no indications of nitrogen whatever, and the other two only ·018% and ·0023.% The average of the whole being ·0020%, an amount which may be considered as quite inappreciable in influencing the quality of steel in the slightest degree. Then come two experiments on Bessemer steel; both these show nitrogen, one to the amount of ·007%, and the other ·011%. In both these cases, large quantities (50 grm. to 55 grm.) were used, and it may be possible that this peculiar kind of steel contains some small quantity of nitrogen; though, even in this case, the nitrogen would not affect its quality, being most likely an accidental constituent, formed during the process of manufacture, from the stream of air driven through the molten iron forming some compound in it analogous to that which nitrogen forms with titanium, and which is so often found in crude pig irons.

Then follow four experiments upon specular iron, which show, with one exception, a total absence of nitrogen. One of these must be particularly alluded to, viz., No. 52, in which 80 grm. were submitted to experiment for four hours. At the end of this time it was found that no nitrogen whatever had been eliminated. This we look upon as one of the best and most conclusive experiment we have made, and its evidence is very strong in favour of the conclusion that nitrogen is not essentially present in steel. The two experiments which remain to be mentioned were made upon iron of English manufacture, of very soft quality, and the same converted into steel by heating to full redness in a current of carbonic oxide. In both cases the result was so small as to indicate mere traces of no importance.

These are the experiments we have to lay before you, and, after reviewing the whole of them, the only just conclusion that can be arrived at is that nitrogen does not exist, either in steel or in iron, as an essential constituent, and cannot therefore be made use of to explain the different commercial qualities of those substances. Altogether there are twenty-two experiments, upon which we can fairly place reliance, as containing no manifest error, and of these thirteen gave absolutely no nitrogen. Of the remaining nine, six do not exceed one-hundredth per cent., and of the other three, one gives only eighteen, one only fifteen, and the remaining one no more than eleven-thousandths per cent. of nitrogen.

Taking the average of the whole, it amounts to but ·0033%, a result which we submit is practically of no value. The adhesion of air to the surface of the steel would be sufficient, in most cases, to explain the amounts which, in some instances, were obtained, and in experiments carried to such a nicety, this source of error must not be overlooked. This, and that arising from the air remaining in the apparatus, small as its amount may have been, are quite sufficient, in our opinion, to account fully for all the nitrogen obtained. It is not of course to be expected that in a long series of experiments, every one should be as successful as could be wished; but we have laid these before you, good and bad, as they occurred, rejecting only such as contained a manifest and palpable error, and from the whole we give it as our opinion, that nitrogen is not an essential constituent of steel or iron, that it very rarely exists in them even as an accidental constituent, and that it has nothing whatever to do with the respective qualities of different samples of those substances.

Without at all wishing to undervalue the researches of others, we may express a doubt whether the nitrogen they obtained in their experiments was not altogether derived from those sources of error we have pointed out, and which we ourselves found it difficult to guard against entirely. At the least we may state that, in our hands, the method adopted by M. Frémy for estimating nitrogen in iron has led to different results.

## XLVII.—*On the Separation of Monochloracetic and Dichloracetic Acids.*

By Hugo Müller.*

In a memoir published a few years ago,† I described the preparation of various products of substitution, and, with relation to the action of chlorine on acetic acid, I pointed out that, in presence of iodine, the chlorine acts upon acetic acid in such a manner as to produce monochloracetic acid, which, in its turn, is transformed into an acid liquid, which I regarded as dichloracetic acid.

In the course of my researches on malonic and succinic acids, the principal results of which have been recently published,‡ I proposed to extend my observations to dichloracetic acid itself, and as M. Maumené has recently communicated a paper on this acid to the Chemical Society of Paris,§ I am induced to bring before the notice of chemists the observations which I have myself recently made on mono- and di-chloracetic acids.

The action of dry chlorine on crystallisable acetic acid is remarkably facilitated by the presence of iodine, to such a degree indeed, that the influence of sunshine is no longer necessary. I have made use of monochloracetic acid prepared in this manner to effect the conversion of acetic into malonic acid. I soon found out that the crystallisable acetic acid may be advantageously replaced in this process by an acid mixed with such a quantity of water as not to solidify at temperatures near 0°,—an observation likewise made by Maumené.

---

* Bull. Soc. Chim. de Paris, 1864, p. 126.

† Chem. Soc. J., xv, 41.

‡ Bull. Soc. Chim. de Paris, 1864, p. 167.

§ Ibid., 1864, p. 417.

Into a *retort-flask* having a very long neck, I introduce half a litre of acetic acid, and from 40 to 60 grammes of iodine. The chlorine is introduced by a tube passing into the interior of the flask, and the hydrochloric acid escapes by a lateral neck proceeding from the upper part of the apparatus. The acid which forms on applying heat to the liquid, condenses in the vertical neck, so that the use of a refrigerator may be dispensed with.

The action of the chlorine does not become rapid till the moment when the iodine passes to the state of perchloride.

When the chlorine passes in at a moderate rate, the whole of it is absorbed, and, in a well-conducted operation, nothing but hydrochloric acid escapes.

If the current of chlorine is too slow, part of the iodine is set at liberty, and sublimes in the neck of the apparatus. On accelerating the current of chlorine, the iodine passes to the state of protochloride, which flows back into the flask, where it is quickly converted into perchloride, and then the action on the acetic acid begins. These phenomena afford the means of regulating the operation. After the action of the chlorine has been continued for some days, the stream is interrupted, and the ebullition of the liquid is prolonged till the vapours exhibit a violet colour, arising from the presence of free iodine. The flask is then left to cool, and the liquid is decanted and distilled. When the temperature has risen to 180°, the greater part of the iodine is found to be eliminated, together with the unaltered acetic acid; this portion of the distillate may be again submitted to the action of the chlorine. The portion which distils between 180° and 188° crystallises on cooling, and after repeated distillation and crystallisation, yields pure monochloracetic acid.

A certain quantity of iodacetic acid is always formed during the reaction, and this acid, being decomposible by heat, gives rise to the separation of iodine-vapours during the distillation. This production of iodacetic acid constitutes the only inconvenience of the mode of preparation just described, but for the greater part of the uses to which monochloracetic acid may be applied, this circumstance is not detrimental. The iodacetic acid may, however, be got rid of, either by repeated distillation, or by turning to account the reaction mentioned by Kekulé, that is to say, by decomposing the iodacetic acid with a small quantity of concentrated hydriodic acid.

The portion of liquid which remains after the temperature has risen to 188°, is more or less considerable according to the duration of the action; in the most favourable case, it is equal to the quantity of monochloracetic acid obtained. As chlorine appears to act on monochloracetic acid more easily than on acetic acid itself, it is advisable, if monochloracetic acid is the only product sought, to stop the operation at the end of 60 hours at the furthest.

The portion which has not distilled at 188° consists chiefly of dichloracetic acid, but likewise contains some iodated acetic products, which may, however, be eliminated in the manner above described for the purification of monochloracetic acid. The residue subjected to repeated fractional distillation, easily yields dichloracetic acid having a constant boiling point. A small quantity of hydrochloric acid is always evolved, arising from decomposition, but the quantity of dichloracetic acid thus decomposed is insignificant.

Dichloracetic acid boils at 195°. I have distilled as much as 500 grammes of it, without observing a variation of more than 2° in the boiling point during the entire course of the distillation. It is highly corrosive, and when heated emits a characteristic suffocating odour.

I have not succeeded in solidifying dichloracetic acid by cold, but I have not tried the method described by Maumené.

Dichloracetic acid appears to be readily decomposed by water, hydrochloric acid being quickly formed, and the liquid, after neutralisation by ammonia, yielding a precipitate with chloride of calcium.

The dichloracetates are, for the most part, easily soluble in water; those of the *alkali-metals* crystallise with difficulty; so likewise do the *lead-* and *barium-salts.* The *lead-salt* evaporated to dryness, yields a colourless, transparent, resinous mass, soluble in water, but insoluble in alcohol. — The *silver-salt* forms small, white crystals confused, and difficult to determine. The solution of these crystals quickly turns brown, depositing chloride of silver and metallic silver. This phenomenon, having been observed in mother-liquors which had been kept to themselves for some time, may perhaps have been due to the presence of a small quantity of trichloracetate.

*Dichloracetate of Ethyl* is obtained by passing dry hydrochloric acid gas into absolute alcohol holding dichloracetic acid in solution. It forms a dense liquid, which boils at 156°, but always with slight decomposition. Strong ammonia, and even dilute alkalis, decompose it, with evolution of heat.

*Dichloracetate of Methyl* is obtained in the same manner as the ethylic ether. The two ethers are very much alike, having an agreeable aromatic odour, and a saccharine taste.

The liquid which remains in the retort, and does not distil till the temperature has risen to between 195° and 210°, appears to contain trichloracetic acid. When heated with concentrated ammonia, it yields, amongst other products, an oily liquid, possessing all the characters of chloroform; but I have not been able to extract crystallised trichloracetic from this residue.

In conclusion, I may observe that in the ordinary preparation of monochloracetic acid, there is formed also a small quantity of dichloracetic acid, as shown by the analysis of the ethereal products obtained by Mr. Foster.

## XLIX.—*On the Nature of the Compound Ethers.*

By J. Alfred Wanklyn.

The most convenient way of expressing the fact suggested by the action of sodium upon valerianic ether is to designate valerianic ether by the name Ethylate of Valeryl. It is thereby implied that, in the majority of reactions into which valerianic ether enters, the valeryl, and not the ethyl, is the portion which is exchangeable.

It is to be expected that this mode of reaction is very general, occurring, not only with the ethers of mono-basic, but also with those of poly-basic acids; and perhaps one of the most serviceable classifications of the compound ethers will turn out to be one based upon this general fact, according to which they will range themselves into three classes:—

Class I. Compound ethers wherein the acid-forming radicle is usually exchangeable.

Class II. Compound ethers wherein the alcohol-forming radicle is usually exchangeable.

Class III. Compound ethers wherein acid-forming and alcohol-forming radicles are about equally exchangeable.

It will of necessity require an immense accumulation of facts before a thorough satisfactory assignment of the numerous compound ethers to these classes can be made; but, nevertheless, it seems to me that a provisional assignment may be attempted with the employment of the data which are at present accessible.

To the first class will belong:

The ethers of the fatty acids, *i.e.*,
" " aromatic acids.
" " oxalic acid.
" " boracic acid.
" " silicic acid.
" " carbonic acid, &c.,

and of course many other sets of ethers which I am unable, at present, to specify.

The characteristics of these ethers of the first class are:—

(1) With alkali-metals there is replacement of the acid-forming radicle—wholly in the case of the mono-basic, and either wholly or partially in the case of the poly-basic.

(2) With organo-metallic bodies, such as zinc-ethyl, or sodium-ethyl, there is replacement of the acid-forming radicle by metal, and formation either of a ketone or else, in the case of poly-basic ethers, of a *reduced acid.*

(3) With potash (alcoholic solution) always an alcohol, never an ether.

(4) With ethylate of potassium, no reaction.

(5) With ammonia, an amide of the acid-forming radicle.

To the second class will belong:—

Iodides.
Bromides.
Chlorides.
Nitrites.
Nitrates.
Fluorides (?)

Characteristics of second class :—

(1) With metals—alcohol-radicle, or else organo-metallic body.
(2) With organo-metallic body—alcohol-radicle double.
(3) With potash in alcohol—ether as well as alcohol.
(4) With ethylate of potassium—double ether.
(5) With ammonia—compound ammonia.

In making out the third class, it is matter for consideration whether the classification might not (with advantage) be widened, so as to include all ethers, and not merely the so-called compound ethers. If this be done, common ether and its homolgues, also the double or mixed ethers, and the anhydrides, will belong to the third class.

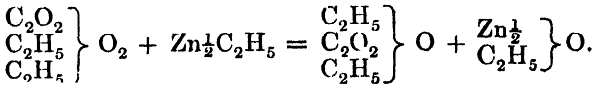
I will now proceed to discuss some of the ethers which have been assigned to the first class. Passing over the ethers of the fatty and aromatic acids, the ethers of oxalic acid will first claim attention.

Oxalic ether, ethylate of oxalyl, is known to evolve carbonic oxide when it is heated with sodium. Carbonic oxide is the product of the splitting up of oxalyl.

Frankland and Duppa's admirable research on the action of zinc-ethyl on oxalic ether supplies the material for deciding whether that ether possesses the second characteristic.

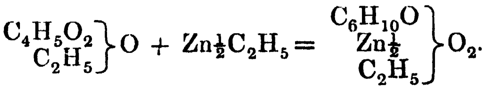
Here follows a representation of the reaction :—

(1.)....



$$\left.\begin{matrix}C_2O_2\\C_2H_5\\C_2H_5\end{matrix}\right\} O_2 + Zn\tfrac{1}{2}C_2H_5 = \left.\begin{matrix}C_2H_5\\C_2O_2\\C_2H_5\end{matrix}\right\} O + \left.\begin{matrix}Zn\tfrac{1}{2}\\C_2H_5\end{matrix}\right\} O.$$

(2.)....



$$\left.\begin{matrix}C_4H_5O_2\\C_2H_5\end{matrix}\right\} O + Zn\tfrac{1}{2}C_2H_5 = \left.\begin{matrix}C_6H_{10}O\\Zn\tfrac{1}{2}\\C_2H_5\end{matrix}\right\} O_2.$$

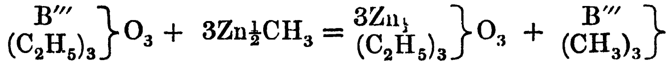
I have divided the reaction into two successive stages for the sake of clearness, and have employed a half atom of zinc ($Zn\tfrac{1}{2} = 32{\cdot}5$).

The first equation is quite in accordance with the rule, *e.g.*, zinc replaces half of the acid-forming radicle, and produces ethylate of zinc; at the same time ethyl combines with the half-acid-forming radicle which was set free, and so a reduced mono-basic ether results.

The second equation takes place in obedience to the law sketched out by Kekulé, viz., that an acid is in a state of stability when the number of atoms of oxygen in the acid radicle is equal to the number of atoms of hydrogen which are replaceable by metals. The acid-forming radicle $C_4H_5O_2$ not being balanced by the presence of two atoms of replacable hydrogen, or of metal, or of alcohol-radicle, offers a point of easy attack to the zinc-ethyl, and so a case of reduction occurs as a secondary action.

Oxalic ether is well known to present characteristics 3, 4, and 5.

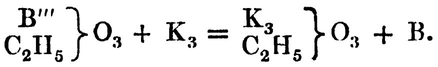
Respecting the relations of boracic ether, or ethylate of boron, I am likewise indebted to the researches of Frankland.



$$\left.\begin{matrix}B'''\\(C_2H_5)_3\end{matrix}\right\}O_3 + 3Zn\tfrac{1}{2}CH_3 = \left.\begin{matrix}3Zn\tfrac{1}{2}\\(C_2H_5)_3\end{matrix}\right\}O_3 + \left.\begin{matrix}B'''\\(CH_3)_3\end{matrix}\right\}$$

Here the acid-forming radicle boron changes against zinc, giving ethylate of zinc and methide of boron, which is exactly in accordance with the rule.

What the action of potassium or sodium on ethylate of boron is, cannot yet be stated as a fact demonstrated by experiment, but I expect it will turn out to be



$$\left.\begin{matrix}B'''\\C_2H_5\end{matrix}\right\}O_3 + K_3 = \left.\begin{matrix}K_3\\C_2H_5\end{matrix}\right\}O_3 + B.$$

In conclusion, I would again refer to Löwig and Weidmann's memoir "On the Action of Potassium and Sodium on some Salts of Ethyl," which was published in 1840.*

In this memoir the action of potassium or sodium upon formic ether, acetic ether, and benzoic ether was described. It was clearly made out that ethyl was not evolved, but that "æther-kali" was produced. So far the results obtained in 1840 seem to be correct.

The difference between the views which I have now, in 1864, to bring forward and the views of 1840 relates to the acid-forming portion of the ethers.

Precise and definite replacement of an acid-forming radicle, with occasional secondary action, is the rule to-day; in 1840 it was the old fashioned irregular reduction. But, notwithstanding the mythical nature of many of the products described by them, still

---

* Pogg. Ann. vii, 95, et seq.

**Löwig** and **Weidmann** were right as to the main fact, and this memoir must be pronounced to have been far in advance of its time, and to consitute one of the landmarks of organic chemistry.

## L.—*Remarks on the Brine of Salt Meat, and on the Distribution of Albumen through Muscular Tissue.*

### By WILLIAM MARCET, M.D., F.R.S.

ON considering Professor Graham's remarkable discoveries on liquid diffusion, it appeared to me that the process of dialysis might be available to separate the salt from the brine of salt meat, in order to obtain from it a liquid which might be used as soup. I accordingly commenced, in November, 1862, some experiments on the subject, and soon found that by evaporating brine to about one-third of its bulk, decanting the mother-liquor after the crystallization of the salt, and dialysing the liquor for from 18 to 36 hours, the liquid remaining on the dialyser possessed a strong taste of soup, and none but the amount of salt necessary for flavour; in fact, it could hardly be distinguished from soup prepared in the usual way. Under the impression that cheap soup obtained by this method might be used as a means of assisting in the relief of the distressed Lancashire operatives, I communicated on the subject with a friend at Liverpool, who was actively engaged on this benevolent undertaking, and sent him samples of brine-soup. His answer was not, however, so favourable as I had anticipated; moreover, on considering further the process for the preparation of the soup, it became obvious to me that although this liquid possessed the smell and taste of broth, it was necessarily poor in nutritious qualities, being deficient, in a great measure, in the crystalloid constituents of the juice of flesh. Thus phosphates, lactates, kreatine, and kreatinine, crystalloids which are present in flesh, and pass into the brine during the process of salting, must be lost to a great extent while the brine is being dialysed. From these and other considerations I then gave up my intention of publishing the above method for preparing brine-soup. Previously, however, on the 14th February, 1863, an article appeared in the "Family Herald" under the title *Utilization of Brine*, stating shortly, but clearly, that I had found a method for extracting soup from brine, the process being the application of dialysis to the brine of salt meat. I was much annoyed at this article, which was published entirely without my knowledge or sanction.

It is no way remarkable that during the ordinary process of salting meat, a considerable proportion of its crystalloid constituents should diffuse into the brine, and that the salt of the brine should, from its known diffusibility, readily permeate the meat. Thus it is that brine which has been used for salting meat is charged with phosphates, lactates, kreatine, and kreatinine. It occurred to me that this liquid might be a good source for the preparation of lactic or sarco-lactic acid and kreatinine, when comparatively large specimens of these substances are required. Liebig has demonstrated their presence in brine, but he failed to extract kreatine from it, on account of the difficulty of isolating this substance from chloride of sodium. The following method, I adopted, differs somewhat from that recommended by Liebig for the extraction of the constituents of juice of flesh. It enabled me to obtain kreatine in small quantity from brine in addition to the two other substances.

Brine, obviously rich in juice of flesh, was boiled and filtered to remove the albumen, then concentrated to about one-fourth of its bulk, and allowed to cool, when a considerable proportion of the chloride of sodium crystallized. The liquid was then decanted and mixed with alcohol, which was added as long as it caused in the fluid a precipitate. The liquid filtered from this precipitate contained the lactates, kreatinine, and most of the kreatine. After distilling off the alcohol, the residue was mixed with a concentrated solution of chloride of zinc; and some weeks later a mass of crystals had formed in the fluid, consisting of *lactate of zinc*, the *double chloride of zinc and kreatinine*, and *kreatine*. These crystals were collected on a filter, washed with a very small quantity of cold water pressed between folds of filtering paper, and dissolved in water. The solution filtered from some oxide of zinc contained in suspension was now boiled with hydrated oxide of lead, and again filtered. This last filtrate contained the kreatinine and kreatine; the lactic acid had remained on the filter as an insoluble lead salt. In order to obtain the lactic acid under the form of lactate of lime, I decomposed the lead precipitate with sulphuric acid, then neutralized the fluid with carbonate of lime, and, after filtration, removed the dissolved sulphate of lime by the addition of alcohol.

The fluid yielded on evaporation a mass of crystals, which, on analysis, proved to be nearly pure lactate of lime. In order to separate the kreatine from the kreatinine in the filtrate from the lead precipitate, the fluid was evaporated to dryness, and the residue treated with alcohol which dissolved out the kreatinine and left the kreatine. The latter was obtained crystallized from its subsequent solution in water, and the former from its solution in alcohol.

Another peculiarity in the composition of the brine of salt meat has attracted my attention,—this is the large proportion of albumen it contains. At first sight it may appear very natural that the albumen of the juice of flesh should pass out into the salt water with the other soluble constituents of meat; but on a further consideration the phenomenon has appeared to me very remarkable, as it does not apparently agree with the known laws of diffusion. A mass of flesh, in so far as its physical properties are concerned, would be classed as a colloid body; for other parts of the animal body also organised, as membranes, are used as colloid septa, being essentially colloid bodies; albumen being a colloid substance, we have here apparently the case of a colloid diffusing very readily through a colloid mass, which is in opposition to the laws of diffusion. I thought at first that the albumen of the juice of flesh might perhaps be peculiarly possessed of the property of passing through a membrane like a crystalloid; but having placed some juice of flesh in a piece of pig's intestine,* and immersed the whole in water, in one experiment I could not observe any diffusion of albumen out of the membrane after 24 hours, and in another there was merely a trace of albumen in the water. I obtained a similar result by placing some juice of flesh in a dialyser supplied with a parchment-paper diaphragm, and floating the dialyser on water. I then instituted the following experiment:—A piece of fresh raw beef was placed in a tall and narrow jar, and allowed to remain undisturbed for two days; being then examined, it was found that the water up to the level of the upper margin of the meat had turned red; the water above the meat was divided into four horizontal layers by strips of paper gummed to the glass, and each layer was decanted in succession with a syphon. The first and second layers on being tested, gave no trace of albumen; the third layer yielded a very slight haziness by the application of heat and nitric acid; the fourth layer yielded a decided haziness, though no distinct coagulation. The coloured fluid now decanted, on being boiled and with nitric acid, showed that it contained a large quantity of albumen. Consequently in this experiment the albumen had diffused readily out of the meat, but the water, within certain narrow limits, had opposed an invincible obstacle to its further diffusion. In the following experiment, water was replaced by gelatin. I immersed a piece of fresh muscle in a solution of isinglass just before it solidified. The next day there was not the slightest coloration of the jelly, even close to the meat, from which it may be concluded that no albumen had passed out; gradually, however, the gelatin round the meat became slightly coloured, and on the sixth or seventh day, each fragment of meat was surrounded by a red zone which did not however permeate the whole of the jelly. The coloured isinglass was found, on being tested, to contain albumen, but not near so much as if the muscle had been immersed in water; from this experiment it may be concluded that gelatin at first checks completely the exit of albumen from muscle, but after a time this substance passes out, although to a very limited extent; and moreover, it is shown that albumen has but a very slight tendency to travel through gelatin. These results all agree perfectly with those obtained by Graham, who considers albumen as an essentially colloid substance.

---

* The pig's intestine had been dried for its preservation. I had softened it in water at the time the experiment was undertaken.

The next point was to determine the physical nature of muscular tissue, and for this purpose I transformed a piece of muscle into an unmistakable colloid mass by mincing it finely, and triturating it afterwards in a mortar with a fluid solution of isinglass. The mass was afterwards placed in a wide beaker and allowed to gelatinise; a thin layer of water was then poured carefully over the jelly. Two days later the water was very pale red coloured, and on the application of heat and nitric acid, a haziness took place, changing into a few flakes of coagulated albumen; this quantity of albumen was exceedingly small. After five days the liquid was smelling a little from decomposition; it contained a little more albumen, but the quantity was in no respect to be compared with that which passes out of pure muscle into water. From this experiment it follows, that muscular tissue, when transformed into a colloid, loses, in a very great measure, its property of allowing the albumen it contains to pass out into water, consequently *a muscle is not a colloid mass.*

Muscular tissue consists of bundles of fibres connected together by means of cellular tissue; a fluid being distributed throughout muscle may therefore be considered as having to pass through an immense number of delicate membranes and innumerable cellular spaces. I have shown that a common membrane, such as a piece of intestine preserved in the dry state, does not let albumen through it; but would a very delicate animal membrane have the same property? As I was reflecting over this question, an experiment I had performed shortly before gave me a clue to its answer. I had selected as a dialyser the cellular or fibrous membrane which covers the liver of the ox and the sheep;* this is an exceedingly fine membrane perhaps not thicker than goldbeater's skin; having removed a small quantity of this tissue from the liver of the ox, I had made it into the diaphragm of a dialyser by causing it to adhere to the rim of the wide opening of a glass filtering-funnel; the diameter of this dialysing septum was 7 centimetres; 10 cc. of a fluid extract of flesh had been introduced into the funnel, and the membrane placed in contact with the surface of a small quantity of water. Twenty-four hours afterwards the water was slightly coloured red, and on boiling it a few flakes of albumen appeared; this was certainly an indication that albumen passed through a fine delicate membrane more readily than through that of the intestines.

A similar experiment had been also undertaken with a still finer membrane, that covering the liver of the sheep; in this case the diameter of the diaphragm was 4·5 centimetres, it adhered firmly to the rim of a small funnel, into which I introduced 5 cc. of an aqueous extract of flesh, and the membrane was placed in contact with the surface of a small quantity of water. The experiment was begun immediately after the membrane had been removed from the liver; it was then quite fresh and moist, whilst it had been allowed to dry in the former experiment. Eighteen hours afterwards the water was slightly red; on boiling, it first became muddy, and then flakes of albumen appeared. I determined, approximately, that about one-third of the albumen in the dialyser had passed out into the water. In a last experiment, I made a dialyser with a test-tube, the bottom of which had been broken, and I fastened a small piece of a still more delicate part of the membrane of sheep's liver to the rim of the tube. Some extract of flesh was introduced into the tube, and the membrane placed in contact with a little water; the water began very quickly to turn coloured, and, on testing it four hours after the beginning of the experiment, I found it charged with albumen.

---

* The liver has two membranes, one which covers it entirely, and another—the peritoneum—which incloses it but partly. I used indifferently these two membranes, together or separately.

These experiments appear to me very interesting, as showing that albumen passes readily through a very thin animal membrane into water; and we may expect that it is by a similar process that albumen is able to pass through the infinite number of delicate membranes which form the walls of the muscular cells; it can be admitted that the fluid travels inside the cells by capillary motion.

I now applied myself to determine the reason of this passage of albumen through a very thin membrane,* and from a suggestion of Prof. Graham, I was induced to examine very closely the membrane of the liver I had used as a dialysing septum, in order to ascertain whether it exhibited any rupture or breach of continuity through which albumen might accidentally have passed. The result of this inquiry was that after macerating the liver in water for some hours, its membrane can be detached without difficulty, and in a perfectly sound condition, as far as can be ascertained by a very careful ocular examination—that when fastened to a dialyser, water being poured upon it, filters through the membrane, the latter becoming studded on its free surface with minute specks of water gradually running into each other, and after a time forming drops. In one experiment the column of water in the dialyser was 25 millimetres (say one inch) in height, and the diameter of the membrane 24 millimetres; 22 minutes after the water had been poured into the dialyser the first indication of moisture appeared on filtering paper placed in contact with the under surface of the membrane. The first drop fell from the membrane 4 hours later; the fall of the second drop was hastened by an accidental blow to the table; the third drop fell 1 hour and 35 minutes after the second. We may, therefore, conclude that the fine membrane experimented upon had not been torn or otherwise injured, but was *porous*, and on this account allowed a fluid to pass through it.

---

* I stated before the Chemical Society I considered this phenomenon one of liquid diffusion: according to a suggestion from Professor Graham, I instituted the additional series of experiments reported in the present paper communicated in the following meeting of the Chemical Society), from which it will be observed I have found the process to differ from that described by Graham as liquid diffusion.

The rate of transition of albumen through the membrane of the liver into water was ascertained by fixing the membrane to the rim of a common size test-tube, the bottom of which had been cut off, introducing five cubic cent. of an extract of flesh (the albumen of which had been quantitatively determined) into this dialyser, and placing the diaphragm in contact with five cubic cent. of water. After 17 hours, 1·6 cubic cent., or 32% of the albuminous fluid, had passed into the water, and exactly 32% of the albumen was found to have travelled through the membrane into the water. The amount of albumen, and the volume of fluid which had escaped out of the tube, were, therefore, exactly proportional. This shows not only the rate of passage of albumen through the membrane, viz., 32% in 17 hours, but also that the process is one entirely of transition through small apertures, and not of liquid diffusion.

In order to inquire further into the passage of albumen through the membrane of sheep's liver, I made an experiment, which unexpectedly yielded a very interesting result. I thought of turning the liver itself into a dialyser, the tissue of the gland being abundantly supplied with albumen. A surface of the gland enclosed in its membrane was immersed in distilled water, and I observed in this case, that some albumen found its way into the external water, although less than when the membrane had been removed from the gland. A comparative experiment was made by immersing in equal bulks of water a part of liver enclosed in its membrane, and a section of the liver; the latter being consequently not covered by membrane, the surface of the section was about one-half that of the liver immersed with its membrane. The next day, at the same time, I interrupted the experiment and determined the albumen in 20 cubic cent. of each fluid—0·0695 grms. of albumen was found to have passed through the membrane for every 20 cc. of the external fluid, and 0·118 grms. of albumen had exuded directly from the tissue for every 20 cc. of the external fluid. But as the surface of the membrane was about twice that of the section, it follows that for equal surfaces bathed in equal bulks of water, about four times as much albumen would have passed out of the section as out of the surface covered with membrane.

Now why does the membrane let albumen through it more readily when removed from the liver than when adhering to it?

As I hope to have shown satisfactorily that the membrane can be separated from its gland without being torn or injured, and moreover, that this membrane in its sound condition is *porous*, I believe the question only admits of one explanation, namely, that when forming part of the liver, the membrane is coated with a colloid substance, which occupies its pores more or less, and extends into the substance of the liver, causing it to adhere firmly to the tissue of the gland, as if it were pasted upon it. This view is supported by the following facts :—

1st. In its normal condition the membrane adheres strongly to the tissue of the gland, but after soaking in water it can be easily removed from it.

2nd. On pealing off the membrane it is difficult to prevent some of the tissue being torn away with it.

3rd. The membrane itself appears as if containing a substance like glue, which causes it to adhere very firmly to glass when dried in contact with it.

4th. The membrane when dried is much less pervious to water than in the fresh moist condition, as if a substance had dried within its pores, which required to be dissolved, in order to enable liquids to pass through.

I am not prepared to state whether this colloid substance, if its existence be considered as proved, is equally distributed throughout the gland or not; but its presence under the above conditions appears to me a remarkable circumstance in a physiological and chemical point of view.

Considering the results of these experiments, it now appears little doubtful that the distribution of albumen through muscular tissue takes place by a process of porous imbibition, as in the case of the membrane; the travelling of albumen through muscle must therefore be considered mainly or entirely as a phenomenon of *physical distribution,* due to *porosity,* and not of liquid diffusion.

In order to judge whether the passage of albumen through muscular tissue is in any degree a phenomenon of liquid diffusion, I determined, in the following experiment, the relation between the quantity of albumen, and of the crystalloid substance *phosphoric acid,* which diffuses from muscle into water within a given time, and compared the result with the relation between the quantity of albumen and phosphoric acid contained in juice of flesh. It was necessary to begin by determining the proportion between albumen and phosphoric acid in juice of flesh, which was done in the following way. An extract of 200 grms. of beef, well minced, was prepared with 125 cc. of distilled water; I determined the quantity of albumen and phosphoric acid contained in measured samples of the extract, the albumen being coagulated by heat and dried on a weighed filter. The phosphoric acid was estimated by evaporating to dryness a known bulk of the extract, incinerating the residue with spongy platinum, dissolving the ash in acetic acid, and precipitating the phosphoric acid with acetate of peroxide of uranium; precipitation as triple phosphate of ammonia and magnesia could not be adopted, Liebig having shown that phosphoric acid in flesh exists, partly as bibasic phosphate, partly as tribasic phosphate of potash.

On the other hand, I poured 125 cc. of distilled water into a beaker containing 200 grammes of fresh beef, free from fat, and allowed the beaker to remain undisturbed for a certain time, after which the albumen and phosphoric acid were determined in the external fluid in the same way as had been done in the extract. If the result of the experiment showed that the proportion of phosphoric acid to the albumen in the extract was the same as the proportion of the phosphoric acid to the albumen in the water in which meat had been soaked, then it would be obvious that albumen travels through flesh with the same speed as a crystalloid, in which case flesh might be considered exclusively as a porous mass; but if these proportions should respectively differ, there being less albumen in the external fluid in proportion to the phosphoric acid it contained than in the extract (in proportion to the phosphoric acid in the extract), then we would conclude that a muscle allows of a certain amount of *liquid diffusion* throughout its substance, being therefore to some degree a colloid; we shall see that such is the case. The results are as follows:—

| | In 100 cc. extract. | | In 100 cc. external fluid after 26 hours. | |
|---|---|---|---|---|
| Phosphoric acid.. | 0·233 | Prop. 1 : 12·5 | 0·169 | Prop. 1 : 6·3. |
| Albumen ...... | 2·925 | | 1·067 | |

The conclusion from this experiment is, that, at the common temperature, the rate of distribution of the colloid substance, *albumen*, through and out of muscular tissue, is only equal to about one-half the diffusibility of the crystalloid substance, *phosphoric acid*, probably under the form of phosphate of potash, through and from muscular tissue. Therefore a muscle opposes some obstacle to the ready passage of colloid substances, such as albumen, throughout its tissue, which obstacle does not occur in the case of phosphoric acid—a crystalloid, consequently a muscle, in addition to its porosity, is, to some (a slight) degree, possessed of the characteristic property of a colloid mass.

By means of the ready distribution of albumen from the blood-vessels into every portion of a muscle, nutriment is perfectly supplied throughout the organ.

On considering the preparation of soup from the action of dialysis on the brine of salt meat, it occurred to me that by enclosing meat in bladders, or in the intestines of the slaughtered animals, and immersing the whole in a saturated solution of common salt, the salt would diffuse itself through the membrane of the bladder into the meat, while the latter would retain nearly the whole of its albumen and other colloid constituents which are lost in the ordinary mode of salting. The salting in bladders would, therefore, be an improvement on the process commonly in use, as meat thus preserved would be more nutritive and better flavoured; moreover, the common process of removing the salt from salt meat to prepare it for cooking, which generally entails a further loss of albumen and other colloids, would no longer be thus objectionable, because, instead of soaking salt meat directly in water, it would be soaked while enclosed in the bladder. After experimenting on the subject, I found that in warm weather the diffusion of common salt through an intestinal membrane into flesh, although occurring very readily, is not rapid enough to prevent the centre of the meat from undergoing a slight decomposition. I was, therefore, obliged to modify the process, and on the 12th May, 1863, I instituted the following experiments :—

Some beef was roughly cut up and divided into four quantities, each weighing 250 grammes. I added to quantity No. 1, 25 grammes, or 10% of salt; to No. 2, 50 gms., or 20% of salt; to No. 3, 75 gms., or 30% of salt; and to No. 4, 100 gms., or 40% of salt. These several samples of meat, with their respective doses of salt, were enclosed in pieces of pig's intestines preserved by drying and moistened at the time, weighed, and immersed in a saturated solution of salt. On the following 12th June, or after the lapse of a month, the brine had a slight red colour, and contained but very little albumen. The meat was withdrawn from the brine and examined; with the exception of sample No. 1, which had become a little lighter, they had all increased in weight The bladders externally had not the slightest smell of decomposition; on examining their contents, No. 1 and No. 2 had no undissolved salt in them, but there was some in Nos. 3 and 4. There was no smell of decomposition inside the masses. Having secured the bladders, they were soaked in pure water, during which time a little albumen passed out. I tasted the samples at various periods within four days from this date, and found that at least three days were necessary to remove the taste of salt. After four days' immersion in fresh water, although the weather was warm, no smell of decomposition was emitted by the meat; it had a good taste, though much like that of salt meat, and had not so much of the flavour of fresh meat as I had anticipated; it was, I thought, more tender than meat salted by the usual process. It must have been richer in albumen and colloid constituents than commonly salted meat, and, I believe, could not have failed to be more nutritious. The result of these experiments is, that meat mixed with about one-tenth of its weight of salt, and salted in bladders, tastes as well, if not better, than meat salted by direct immersion in brine, and it must be more healthy and nutritive.

## LI.—*Additional Experiments on the Density of Certain Minerals.*

By A. H. Church, M.A., Professor of Chemistry, Royal Agricultural College, Cirencester.

(Continued from page 386.)

*Zircon.*—The observation that zircons increase in density without loss of weight when ignited, seems to be due to Henneberg,* though M. Damour has quite recently investigated the subject with greater completeness. Svanberg also experimented with a great number of zircons from different localities, and came to the same conclusion. The greatest increase in density which I have noted has been less than that observed by Damour. Like gadolinite (mentioned further on), zircon, when heated, exhibits a phosphorescent glow, and it is after this glow has occurred that the greatest increase in density is found to have taken place. But though ignition produces these effects, and also more or less complete loss of colour, the density is not invariably thus altered (experiments II. and III. below).* A crystal of zircon which became denser by heating, and which had been previously measured, seemed to have contracted differently in its different dimensions. I have included in the annexed list some of the results obtained by the heating of zircons from different localities :—

---

* Henneberg: J. pr. Chem. xxxviii. 508. (1846.)

| Locality. | Changes of colour. | Density before ignition. | Density after ignition. |
|---|---|---|---|
| I. Green River, Henderson Co., N. Carolina .. | brown to white | 4·515 | 4·540 |
| II. ,, ,, ,, | ,, ,, | 4·667 | 4·667 |
| III. Espailly, France .. .. | aurora-red to colourless | 4·863 | 4·863 |
| IV. Laurvig, Norway .. .. | hair-brown to colourless | 4·658 | 4·707 |
| V. Fredricksvärn, Norway .. | ,, ,, | 4·489 | 4·633 |
| VI. ,, ,, | ,, ,, | 4·395 | 4·438 |

*Gadolinite.*—The attentive study of the action of heat upon minerals can scarcely fail to throw much light upon some of the obscure questions of chemical geology. To take an example, if we find that a mineral is greatly affected, both as to chemical and physical character, by the action of a moderate degree of heat, and that the changes it has thus undergone, seem, so far as one can judge, to be permanent, it would be unreasonable to assign to it an igneous origin. The rare mineral gadolinite will serve as an illustration. When heated, gadolinite loses a little water, and afterwards becomes suddenly and brilliantly phosphorescent, the glow travelling through the mineral with great rapidity. The mineral loses its vitreous lustre in part; it no longer breaks with a conchoidal fracture, but becomes splintery; and its colour changes from black with a greenish shade, to a pale, greyish green; an increase of density† also occurs, and is probably greater than the experiments indicate, since it is difficult to select a large fragment of ignited gadolinite quite free from minute fissures, some of which are internal, so that their effect in lowering the density of the mineral cannot be corrected by placing it in water under the air pump. The results of some experiments on gadolinite may be thus given; the mineral was from the Ytterby locality, near Stockholm :—

---

* Many of these experiments were made in Gore's gas furnace.

† The observation is due to H. Rose.

| | Density. |
|---|---|
| Before ignition .. .. .. .. | 4·223 |
| After ignition, to low redness, but before phosphorescence .. .. .. | 4·275 |
| After intense ignition and phosphorescence .. .. .. .. .. | 4·356 |

Not only does heat cause the remarkable changes just described, but ignited gadolinite, after it has shown the phosphorescent glow, is no longer soluble in acids. After moderate ignition, if the colour has not been destroyed and the glow has not occurred, gadolinite is still attacked by acids. I feel inclined to attribute, partly at least, the increase in density from 4·223 to 4·275 to the loss of water, but I think the further increase from 4·275 to 4·356, can be best explained by supposing a chemical re-arrangement of the constituents of the mineral to occur, of which re-arrangement the glow is an indication; this glow resembles that seen when ammonia escapes from the ammonio-magnesian phosphate during ignition, though in the latter case the change is more profound. In gadolinite it may be nothing more than a molecular change, one of isomerism, for instance, or possibly, though not probably, the passage of a crystalloid into the colloidal condition. The permanent effects of heat on this mineral are, however, so decisive, that it is difficult to conceive of it as originally formed at a high temperature, whatever conditions as to pressure, &c., may be assumed. The deportment of some of the crystallized volcanic minerals at different temperatures deserves careful study.

*Garnet.*—I examined some of the fused garnet beads (referred to in my former communication) six weeks after fusion, and found their density unaltered.

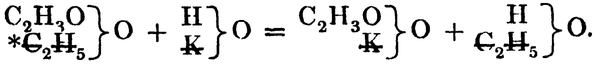
| | |
|---|---|
| Density 1 hour after fusion .. .. | 3·401 |
| Density 6 weeks after fusion .. .. | 3·399 |

The slight difference is due to unavoidable errors of experiment. There is here no tendency towards a return to the higher density of the native garnet previous to fusion, namely, 4·059. When a fragment of iron garnet is enclosed in a cage of platinum wire, and fused, it will be observed that at the moment of fusion the melted mineral bulges out between the bars of the "cage." Afterwards, when the fused garnet has become cold, deep grooves will be found on tearing off the platinum wire, which will have become almost embedded in the melted mass. From this observation it is probable that the diminution of density occurs at the moment of fusion.

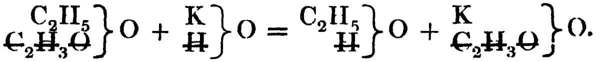
## LII.—*Note on the Action of Sulphydrate of Potassium on Acetic Ether.*

By J. Alfred Wanklyn.

There are two distinct ways of regarding the saponification of acetic ether by potash :—

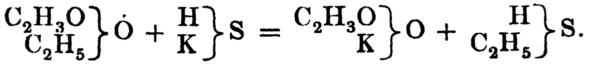
(1.)....


$$\left.\begin{matrix}C_2H_3O\\ {}^*\cancel{C_2H_5}\end{matrix}\right\}O + \left.\begin{matrix}H\\ \cancel{K}\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\ \cancel{K}\end{matrix}\right\}O + \left.\begin{matrix}H\\ \cancel{C_2H_5}\end{matrix}\right\}O.$$

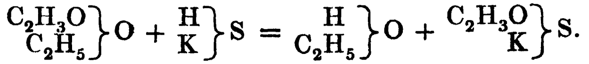
(2.)....


$$\left.\begin{matrix}C_2H_5\\ \cancel{C_2H_3O}\end{matrix}\right\}O + \left.\begin{matrix}K\\ \cancel{H}\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\ \cancel{H}\end{matrix}\right\}O + \left.\begin{matrix}K\\ \cancel{C_2H_3O}\end{matrix}\right\}O.$$

No examination of the products of this reaction can reveal which of these equations represents the truth. But if we substitute *sulphydrate* for *hydrate* of potassium, then we are provided with criterea for distinguishing between them.

(1.) ...


$$\left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\ K\end{matrix}\right\}S = \left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\}O + \left.\begin{matrix}H\\ C_2H_5\end{matrix}\right\}S.$$

(2.). ..


$$\left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\ K\end{matrix}\right\}S = \left.\begin{matrix}H\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\}S.$$

Here are then distinct issues to be brought to the test of experiment. Equation (1)—the customary equation for the representation of reactions of this kind[†] would require acetate of potassium and mercaptan. Equation (2)—the one which the author of this paper considers to be the correct one—requires alcohol and thiacetate of potassium.

---

[*] The crossed symbols are viewed as exchanging places with one another.

[†] In the debate on the paper, when it was read before the Chemical Society, the President seemed to object to equation (1) being termed the customary one. After due consideration, I adhere to the text.

Eight cubic centimetres of pure acetic ether were sealed up with a concentrated alcoholic solution of sulphydrate of potassium* and heated in the water-bath for a long time. On breaking open the tube, there was a slight escape of sulphuretted hydrogen gas, but no smell of mercaptan; neither could mercaptan be detected on distilling off and treating the distillate with oxide of mercury. The non-volatile residue was very alkaline to test-paper, it was neutralized with dilute sulphuric acid, rendered slightly acid and then evaporated to dryness over the water-bath. This residue consisted almost entirely of sulphate of potassium, alcohol not being capable of extracting more than traces of organic salt from it.

The result of this experiment is, that an alcoholic solution of sulphydrate of potassium is almost without action on acetic ether, and that at any rate no mercaptan is formed.

The experiment was repeated twice at higher temperatures than those of the water-bath. (The tube was partially immersed in an oil-bath ranging from 150° to 200° C.) On opening there was a rush of sulphuretted hydrogen, but no smell of mercaptan: the action appearing to be secondary—viz.: first, upon water to form alcohol and acetic acid, which latter would of course liberate sulphuretted hydrogen from the sulphydrate of potassium. Nothing certain was made out concerning the presence or absence of traces of thiacetate.

The non-production of mercaptan, and also the extreme difficulty with which the sulphydrate attacks acetic ether, appear to the author to be evidence against the establishment of equation (1).

Touching the latter point, the question may fairly be raised; inasmuch as even chloride of ethyl acts so readily upon sulphydrate of potassium, why should not acetate of ethyl act readily too if it be a salt of ethyl? Grant that acetic ether is really ethylate of acetyl, and this difficulty vanishes.

---

* The alcohol employed was not absolute. Just the same solution of sulphydrate was taken as that which had given an excellent product when used to make hexyl-mercaptan.

# LIII.—*On Chloro-brominated Ethylene.*

By HUGO MÜLLER.

WHILST searching for a convenient method of preparing chloro-succinic acid, it appeared to me probable that this object might be gained by submitting chlorinated cyanide of ethelene ($C_2H_3Cl(CN)_2$) to the action of caustic alkalies or hydrochloric acid. My expectations, however, were frustrated by the unexpected deportment of bromide of chlorinated ethylene ($C_2H_3Cl\,Br_2$) to cyanide of potassium, which gave rise to the formation of chloro-brominated ethylene, instead of forming the desired cyanogen compound ($C_2H_3Cl\,(CN)_2$.

On heating an alcoholic solution of bibromide of chlorinated ethylene (which boils at 162—164° C) with cyanide of potassium, a reaction soon set in, and a very volatile heavy liquid distilled over along with some hydrocyanic acid. After a short time I noticed the formation of a white substance in the tube of the refrigerator, as well as in the receiver, and the heavy liquid itself was gradually converted into this white substance. This at once reminded me of the monobrominated ethylene, described some years ago by Hofmann.* As, however, the mode of formation made it doubtful that the latter substance would make its appearance under these circumstances, I submitted the white substance I obtained to an analysis, which gave the following results:—

0·2816 substance on being burnt with caustic lime and C., gave
2·6590 silver-compound, which was a mixture of chloride and bromide of silver. 0·6533 of this compound, on being heated in a current of chlorine, lost 0·0831. These results correspond to:
53·51 per cent. of bromine, and 26·78 chlorine.
56·50 bromine, and 25·08 chlorine are the percentages required by the formula $C_2H_2BrCl$.

The results of this analysis are near enough to prove that the substance in question was the chloro-brominated ethylene.

With regard to the transformation of the liquid chloro-brominated ethylene into the solid modification, I have noticed the same peculiarities mentioned by Hofmann in describing the monobrominated ethylene. A mixture of the liquid and solid modification was left standing with some water for more than a year, and yet, on heating the whole in a retort, a considerable quantity of the liquid modification distilled over, which, however, partly solidified in the receiver. By repeated distillation with water I succeeded in converting the whole into the solid modification.

---

* Chem. Soc Qu. J., xiii., 68.

The properties of the solid chloro-brominated ethylene are so exactly like those of the solid modifications of brominated ethylene (Hofmann), dibrominated ethylene (Lennox), and dichlorinated ethylene (Regnault), that I need not describe them.

Liquid chloro-brominated ethylene boils, in contact with water, at 55 – 58° C.; its vapour possesses a somewhat pungent odour, resembling that of benzoylic chloride, and strongly irritates the eyes.

## LIV.—*Remarks on Chemical Nomenclature and Notation.*

By Professor WILLIAMSON.

A COMMITTEE was appointed in the course of last session by the Council of this Society, to consider and report upon the present state of chemical nomenclature, with a view of obtaining criticisms which might aid in remedying, or at least diminishing, the evils which are felt to exist in our present system; and also practical suggestions for developing and extending those parts of our system which are found to work well. Considerable time has elapsed since the appointment of that committee, yet although several of its members have met and discussed chemical nomenclature, it does not seem probable that their labours will bring the question speedily to a decisive point. Under these circumstances, it would ill become any member of the committee to prejudge the question which his colleagues are considering, and to commit himself to any changes in nomenclature, which have not received the sanction of the committee, if he could remain passive pending their deliberations; but other duties render such a passive attitude impossible to many of us, and members of the committee do continue, in their individual pursuits, to exert those various influences by which our nomenclature is being changed.

Being myself engaged in writing an elementary treatise of chemistry, I am forced to abandon the reserve which, as a member of the committee, I should have been glad to maintain on this subject; and I must either give greater consistency and stability to objectionable names, by working them up into the new principles which I have to expound, or else I must do my best towards remedying defects of our nomenclature, by adopting and using such improvements as seem practicable at present.

The result of some careful consideration of the question has been to convince me, that I can with advantage adopt names for the common compounds, which are free from some defects existing in the usual names.

Innovations in nomenclature are, however, very hazardous undertakings; for every attempt to establish new names creates confusion, if it is unsuccessful; and the greater number of such attempts are unsuccessful.

I must explain beforehand that my endeavour is to introduce some order into the present use of terms, by examining the various words used to denote one and the same thing, and selecting those which can be used with most convenience and consistency; and one of the strongest grounds for believing that my proposals may find favour with chemists, and be adopted by them, is that my plan is one for carrying out acknowledged principles more consistently than they are now carried out in our nomenclature, with very little novelty in anything except arrangement.

Not the least remarkable extension which has of late years been introduced into our views of the constitution of mineral bodies is that which sprung, by the study of organic chemistry, from Lourenço and Wurtz's polyethylenic alcohols. These bodies contain the elements of a molecule of ethylenic alcohol, to which the elements of one molecule of oxide of ethylene are added, or two molecules of the oxide to one of the alcohol, or three of the oxide to one of alcohol, &c.

$$\begin{aligned} C_4H_{10}O_3 &= C_2H_6O_2 + C_2H_4O, \\ C_6H_{14}O_4 &= C_2H_6O_2 + (C_2H_4O)_2, \\ C_8H_{18}O_5 &= C_2H_6O_2 + (C_2H_4O)_3. \end{aligned}$$

It is well known that the formation of these bodies has led to the discovery of similar compounds, formed from bibasic organic acids by the removal of the molecule of water from two molecules of the hydrate, such bodies as ditartaric, dilactic acid, diglycollic acid, &c., and Wurtz, in his "Leçons de Philosophie Chimique," has admirably shown that mineral chemistry affords numberless examples of compounds of anhydrous acids with hydrates and other salts; that polybasic acids generally form such compounds; and that the greater number of the salts of silicic, boracic, and phosphoric acid can only be explained by a generalisation of the law which was observed in its simplest form, in the cases of the bibasic alcohols and acids.

Thus from the normal hydrate of phosphoric acid, $PO_4H_3$, acid hydrates are formed, by combining together $n$ molecules of the hydrate, with elimination of not less than $n-1$ molecules of water, and not more than $\frac{3n}{2} - 1$ molecules.

Thus the salts commonly called pyrophosphates, are formed according to the equation $(PO_4H_3)_2 - H_2O = P_2O_7H_4$, and the several varieties of metaphosphates are formed on the type $(H_3PO_4)_n - (H_2O)_n = H_nPO_{3n}$.

There are perhaps no words in use among chemists of which the original meaning was so clear as the word acid, and the correlative word base. They were introduced to describe bodies of opposite properties, which are more or less completely lost, in the salt or compound of acid and base. The process of combination was no doubt judged, from the simple cases of it which were first investigated, to be mere juxtaposition of two molecules to form one molecule of a compound: combinations such as $SO_3 + H_2O = SO_4H_2$, $SO_3 + BaO = SO_4Ba$; $SiO_2 + PbO = SiO_3Pb$.

The progress of research taught us, however, that many processes of chemical combination between two molecules give rise to the formation of two molecules of the product. Thus we know that a molecule of free chlorine, is chloric chloride ClCl; that a molecule of free hydrogen is in like manner hydrichydride HH; and that a molecule of free chlorine combines with one of free hydrogen, to form two molecules of hydric-chloride $ClCl + HH = HCl + HCl$. In like manner we now know, that a molecule of alcohol does not contain a molecule of ether plus a molecule of water, but two molecules of alcohol are formed by the combination of one of ether with one of water. Numberless reactions, originally supposed to be simple combinations, have been proved to be double decompositions.

Laurent and Gerhardt have been two of the most active of modern chemists, in applying this method of reasoning to the explanation of chemical reactions; but one of them fell into the mistake of asserting that all cases of chemical combination, are really double decompositions; and, as a natural consequence of this mistake, he used for the representation of double decompositions the words which belonged and still belong to the reactions of direct combination of which he denied the existence. In fact he systematically applied the term acid to hydrogen-salts, giving the name anhydride to acids, and leaving bases, however anhydrous they might be, entirely unprovided with a corresponding name.

Now I submit that it is not allowable to use any word in a sense inconsistent with its established meaning and use, unless one has the most ample evidence that it cannot again be wanted, and will not again be used, for its original purpose. Words may be considered as the property of the ideas which they are used to denote, and the words "acid" and "base" belong to the idea of compounds of fundamentally opposite properties, which unite to form one or more molecules of a comparatively neutral compound. Gerhardt, no doubt, really believed that the idea was dead, and would not again want its own titles, and he accordingly bestowed them on the next of kin (the most acid salts).

We now see, however, that there are cases of combination between two molecules to form a single molecule of a compound, as well as cases of the breaking up of one molecule, to form two or more less complex molecules; and that processes in which reactions of these kinds occur are both common and fundamentally important; and we are therefore bound to restore these prematurely appropriated words to their original owners. I need only refer to Wurtz's "Leçons" for numberless well-explained examples of salts containing the elements of the acid in the most varying proportions, added to those of a normal salt, and of others containing the elements of a base, added in varying proportions, to those of a salt. Many of these are known to be actually formed by direct combination of acid and base, but of others a similar mode of formation can only be affirmed to be rational and accordant with analogy.

To illustrate my proposition that direct combination of two molecules to form one is not a dead idea, I will give a few of the more important cases of the best known synthetical reactions :—

$$\begin{array}{llll} CO & + Cl_2 & = & COCl_2 \\ SO_2 & + Cl_2 & = & SO_2Cl_2 \\ C_2H_4 & + Cl_2 & = & C_2H_4Cl_2 \\ Hg & + Cl_2 & = & HgCl_2 \\ Zn & + Cl_2 & = & ZnCl_2 \\ NH_3 & + HCl & = & NH_4Cl \\ PCl_3 & + Cl_2 & = & PCl_5 \\ (NH_3)_2 & + H_2SO_4 & = & (NH_4)_2SO_4. \end{array}$$

$$\begin{array}{llll} C_2H_4O & + H_2O & = & C_2H_6O_2 \\ Zn & + CH_3I & = & ZnCH_3I \\ CO_2 & + C_2H_5K & = & C_3H_5KO_2 \\ CO & + HKO & = & CHKO_2 \\ C_2H_4 & + H_2SO_4 & = & C_2H_6SO_4 \\ C_2H_4 & + HCl & = & C_2H_5Cl. \end{array}$$

$$\begin{array}{llll} CO_2 & + HKO & = & CO_3HK \\ SO_2 & + H_2O & = & SO_3H_2 \\ SO_3 & + BaO & = & SO_4Ba \\ SO_3 & + HCl & = & HSO_3Cl \\ SiO_2 & + K_2O & = & SiO_3K_2 \\ SiO_2 & + PbO & = & SiO_3Pb \\ SO_3 & + (C_2H_5)_2O & = & SO_4(C_2H_5)_2. \end{array}$$

I will not extend my list of examples to cases in which a single molecule breaks up, to form two or more molecules; for processes of the kind are so numerous and so familiar to every chemist, that no one can have any difficulty in collecting plenty of them.

By excluding from his system these phenomena of direct combination, and of direct separation, Gerhardt lost sight of the theory of the most fundamental processes of chemical change, viz., the processes of synthesis, and of immediate analysis. There are at the present time some eminent chemists, who seem disinclined to take cognizance of reactions in which types are maintained by double decomposition.

We cannot admit that the acids do not combine with bases, and that their hydrogen-salts are alone entitled to the name acids: for every known acid combines vigorously enough with bases, when brought in contact with them in the liquid state, in which alone their forces can exert themselves.

Oxide of lead is one of the most active of bases at high temperatures, its salts are very readily decomposed by double decomposition; and chemists might just as well limit the word acid to the salts of lead, calling the acids themselves "anplumbates," as say with Gerhardt, that hydrogen-salts are the only acids, and that the real acids are not acids, but only anhydrides. It is one of the most important facts of chemistry that bodies with much oxygen, such as $SO_3$, $P_2O_5$, $N_2O_5$, $CO_2$, $SiO_2$, &c., resemble one another in their general tendency to combine with bodies of the opposite class, containing little oxygen, such as $K_2O$, $Na_2O$, $PbO$, $BaO$, &c., and the word acid belongs to each body of the former class, while the word base belongs to each of the latter.

But it is not only true that the bodies misnamed anhydrides are acids; it is equally true and certain that the hydrogen-salts cannot with any consistency be called acids: for when two hydrogen salts,—say hydric nitrate and potassic hydrate,—react on one another, we cannot call the process a combination of nitric acid with potash, without putting in the back-ground, and to some extent concealing, the fact that water is formed, quite as much as potassic nitrate. Learners of chemistry who have been told that an acid is a thing which combines with a base, naturally and consistently wish to omit any mention of the water in their description of the process, and they have to be told that this supposed acid really is a salt of hydrogen possessing acid properties, and the so-called base is a hydrogen-salt with strongly basic properties, the two on coming together undergoing double decomposition, just as truly as potassic chloride when mixed with argentic nitrate.

I hold that it is inconsistent and highly inconvenient, to apply to the double decompositions which take place between hydrogen salts of acid properties and hydrogen-salts of basic properties, any terms which conceal the fact of their close analogy with other double decompositions; and that the hydrogen-salts ought to be designated by terms similar in form and general arrangement to the terms applied to the salts of other metals. No doubt the hydrogen-salts, with sulphuric, nitric, phosphoric acids, &c., are exceedingly acid in their properties, but so are also in a lesser degree the salts of all the feebly basic heavy metallic oxides with strong acids. Ferric and aluminic sulphate are perhaps as acid in their reactions as the hydrogen-salt of the acid.

It is not really an argument against naming hydrogen salts in a similar manner to other salts to say, that the hydrogen-compounds of chlorine, bromine, &c., are acid in their properties: for the corresponding compounds of all other nearly indifferent or neutral metals are also acid.

Thus we must admit that ferric, ferrous, aluminic, stannic, and many other chlorides, though normal salts, are acid in their properties, and that hydric chloride is another normal salt of very acid properties.

Every consideration seems to me to point to the necessity of our applying the term "acid salt" to those which have got in each molecule an excess of acid; so that the salts $S_2O_7H_2$, $S_2O_3Na_2$, &c. are acid sulphates; the salt $Cr_2O_7K_2$ is an acid chromate; and $P_2O_7H_4$, or $P_2O_7Na_4$ are acid phosphates.

In like manner I propose to apply the term "basic salt" to such only as contain the elements of a base added to those of a normal salt; thus the compounds of plumbic oxide with plumbic chloride, such as $PbCl_2$, $PbO, PbCl_2$, $(PbO)_2$, &c., are basic salts; so also the compounds of mercuric oxide with mercuric chloride. On the other hand I do not propose to apply the term basic salts to bodies like BiOCl, bismuthic oxychloride, or $Fe_2O_2(SO_4)$, ferric dioxysulphate, $Fe_2O(SO_4)_2$ ferric oxydisulphate. So the normal hydrate $Fe_2O_6H_6$ is called ferric hydrate, $Fe_2O_5H_4 = Fe_2O(HO)_4$ is ferric oxyhydrate, $Fe_2O_4H_2 = Fe_2O_2\ (HO_2)$ is ferric dioxyhydrate, and $Fe_4O_9H_6$ is a basic hydrate, tetraferric trioxyhydrate.

It is certainly inconvenient to use names for ordinary purposes which belong exclusively to any one theory, however good, of the constitution of salts. Admitting, as chemists now do, that the atom of mercury weighs 200, the soluble chloride is often called bichloride, instead of being called protochloride, as formerly, in accordance with the formula derived from the smaller atomic weight of the metal. It would be folly to suppose that the conclusions respecting atomic weights which, in their various bearings represent the highest results of chemical science at present, will not in their turn be replaced hereafter by still more accurate views, founded on a fuller investigation of reactions; and it is therefore desirable that we should, as far as possible, use names which may be retained without inconvenience, even if all the theories which we now make use of were swept away, and replaced by others utterly different from them. For this reason it seems preferable to use for the designation of soluble chloride of mercury the term mercuric chloride, which is equally convenient whether we consider it a compound of one atom of metal with one of chlorine, or as one atom of metal with two of chlorine, or whatever formula we give it.

In this case, calomel will be called mercurous chloride, while the oxide, nitrate, sulphate, &c., corresponding to it will be called mercurous oxide, mercurous nitrate, mercurous sulphate, &c.

Indeed the names of this kind for the greater number of salts are so very much simpler and more convenient than any others with which I am acquainted, and admit of being applied so consistently and naturally to all the chief varieties of compounds, that I propose their systematic introduction and use; and a system of names of this kind is the subject upon which I am anxious to gather the opinions of my learned colleagues in this Society, as well as of other chemists.

I must beg leave to put my proposals in an affirmative form, as that seems alone suited to give them the distinctness necessary for their due consideration.

Many common words and signs which I must make use of in my remarks and formulæ are used in various senses, and I must therefore beg leave to mention the sense in which I employ each of them. Atom is the smallest quantity of an element, or group of elements (radicle) behaving like one element, which is supposed to take part in any reaction. Thus—

$H = 1$ represents an atom of hydrogen.
$Hg = 200$ represents an atom of mercury.
$Sb = 122$ represents an atom of antimony.
$O = 16$ represents an atom of oxygen.
$N = 14$ represents an atom of nitrogen.
$C = 12$ represents an atom of carbon.
$CH_3 = 15$ is an atom of methyl.
$CN = 26$ is an atom of cyanogen.
$NH_4 = 18$ is an atom of ammonium.
$SO_2 = 64$ is an atom of sulphurous acid.
$CO = 28$ is an atom of carbonic oxide.
$C_2H_4 = 28$ is an atom of ethylene.

When I wish to speak of that weight of oxygen, nitrogen, carbon, &c., which is called equivalent to one atom of hydrogen, I use the compound symbols $\frac{O}{2}$, $\frac{N}{3}$, $\frac{C}{4}$, meaning half the weight of an atom of oxygen, one-third the weight of an atom of nitrogen, one-fourth the weight of an atom of carbon; and it seems to me inexpedient to use for an equivalent weight of an element, any symbol, other than one based on atomic notation, and directly intelligible in that atomic notation.

Molecule is the smallest quantity of an element, radicle, acid, base, salt, or other compound which is supposed to exist by itself. Thus $Cl_2$, $H_2$, $O_2$, $N_2$, $P_4$, $As_4$, $Hg$, $Zn$, $Cd$ are molecular formulæ of elements; $NH_3$, $C_2H_4$, $CO$, $SO_2$, $(CH_3)_2$, $(CN)_2$, $(NH_4)_2$ are examples of molecular formulæ of radicles.

$H_2O$ water or hydric oxide, $K_2O$ potash or potassic oxide, $K_2S$ potassic sulphide, $(NH_4)_2O$ ammonic oxide, $(C_2H_5)_2O$ ethylic oxide, $Bi_2O_3$ bismuthic oxide, $SnO$ stannous oxide, $PbO$ plumbic oxide, $Fe_2O_3$ ferric oxide, $Hg_2O$ mercurous oxide, $Cu_2O$ cuprous oxide, $HgO$ mercuric oxide, $CuO$ cupric oxide, $C_2H_4O$ ethylenic oxide, are examples of molecules of bases.

$N_2O_5$ nitric acid, $N_2O_3$ nitrous acid, $I_2O_5$ iodic acid, $I_2O_7$ periodic acid, $(C_2H_3O)_2O$ acetic acid, $C_4H_4O_3$ succinic acid, $SO_2$ sulphurous acid, $SO_3$ sulphuric acid, $CO_2$ carbonic acid, $SiO_2$ silica or silicic acid, $B_2O_3$ boric acid, are formulæ denoting molecules of acids.

$HNO_3$ hydric nitrate, $Fe(NO_3)_2$ ferrous nitrate, $Fe_2(NO_3)_6$ ferric nitrate, $Fe_2(SO_4)_3$ ferric sulphate, $Bi(NO_3)_3$ bismuthic nitrate, $H_2SO_4$ hydric sulphate, $HKSO_4$ hydropotassic sulphate, $H_3PO_4$ hydric phosphate, $H_3PO_3$ hydric phosphite, $HNa_2PO_4$ hydrodisodic phosphate, $Fe_2P_2O_8$ ferric phosphate, $Fe_3(PO_4)_2$ ferrous phosphate, $Al_2Cl_6$ aluminic chloride, $HCl$ hydric chloride, $FeCl_2$ ferrous chloride, $BiCl_3$ bismuthic chloride, $PtCl_2$ platinous chloride, $PtCl_4$ platinic chloride, are formulæ of the molecules of salts and double salts.

It will be observed that in these names the basylous constituent comes first, and in the name of the adjective, while the name of the acid or chlorous constituent comes last, and is in the substantive from. There appears some advantage in observing such a rule as this, so that the name of a salt may show which are held to be the basylous, and which are the chlorous constituents. The names of double salts might in like manner give more prominence to the name of a strong than that of a weak base; thus the double sulphate of hydrogen and potassium ought to be called hydropotassic sulphate rather than potassio-hydric sulphate; and in like manner the salt $PbHNO_3$ is plumbic hydro-nitrate rather than nitro-hydrate.

The prefixes *di*, *tri*, *tetra*, *penta*, *hexa*, *hepta*, &c., attached to the name of each constituent in these words, enable us with facility and clearness to distinguish between double salts containing like constituents in different proportions. Thus common sodic phosphate, $HNa_2PO_4$, is hydro-disodic phosphate; the salt $H_2NaPO_4$ is dihydro-sodic phosphate; the salt $NH_4MgPO_4$ is ammonio-magnesic phosphate, and microcosmic salt is hydrammonio-sodic phosphate. Whenever it must be described by a systematic name, the common red chromate $Cr_2O_7K_2$ is potassic dichromate; sodic pyrophosphate, is tetra sodic diphosphate.

The basic plumbic hydrate $Pb_3O_4H_2$ is triplumbic hydrate. Hydrates which are formed by the removal of the elements of water from the normal hydrate, may perhaps be called *subsalts.* Thus if we admit for the normal salts of carbonic, silicic, and stannic acids, the formulæ $CO_4H_4$, $SiO_4H_4$, $SnO_4H_4$, the ordinary salts on the type, $CO_3H_2$, $SiO_3H_2$, $SnO_3H_2$, would be subsalts, and the prefix "sub" ought to be attached to the names of the basic constituents, which are deficient, rather than to the acid constituents. There seems, however, some difficulty in carrying out such a plan. Perhaps it may be simpler to name the number of atoms of basic metal, and of acid, in all cases where the same constituents occur in various proportions. Thus Dolerite, $Mg_2SiO_4$, is dimagnesic silicate; Enstatite, $MgSiO_3$, is magnesic silicate; Magnesite, $H_4Mg_2Si_3O_{10}$, is tetrahydro-dimagnesic trisilicate; Okenite $H_4CaSi_2O_7$ is tetrahydro-calcic silicate.

Similar names give very distinct designations for the various phosphates; thus the phosphates formed by the removal of two molecules of water, or of an equivalent quantity of other base from two molecules of a normal phosphate are diphosphates:

$$(H_3PO_4)_2 - (H_2O)_2 = H_2P_2O_6 \text{ is dihydric diphosphate.}$$
$$CaP_2O_6 \text{ is calcic diphosphate.}$$

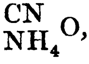
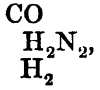
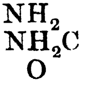
Those formed from three molecules of a normal salt by the removal three molecules of water, are triphosphates:

$$(H_3PO_4)_3 - (H_2O)_3 = H_3P_3O_9 \text{ is trihydric triphosphate.}$$

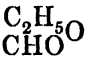
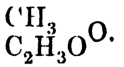
When a metal forms basic as well as acid compounds with oxygen, as in the case of manganese, the former may be called oxides, while the latter are called acids, and the basic oxides may be distinguished from one another by such terminations as manganous oxide $MnO$, manganic oxide $Mn_2O_3$, whilst the acids are similarly distinguished from one another, the words ending in *ous* and *ic*, being supplemented when need arises by others beginning with *hypo*, as now used in the names of the acids of sulphur, or *per*, as in the name of perchloric or permanganic acid.

A neutral oxide, like the body $MnO_2$, now called peroxide of manganese, ought perhaps, in anticipation of its being some day related to salt-like derivatives, to be called *permanganic oxide*. Thus the derivatives of $Pb(CH_3)_4$ would be called perplumbic compounds: $Pb(CH_3)_3Cl$ perplumbic trimethyl-chloride; $Pb(CH_3)_2Cl_2$, perplumbic dimethyl-chloride.

With regard to the use of symbols, such as that of addition, multiplication, &c., there exists among chemists of the present day a most inconvenient and confusing diversity, some chemists even using one and the same symbol in various senses.

It appears to me both practicable and expedient to exclude the sign of addition +, from the composition of every molecular formula, and to employ mere juxtaposition of the letters denoting atoms in designation of every combination. The sign *plus* should be placed between the formulæ of molecules; which are brought together in the reaction which has to be described. Thus $H_2SO_4 + KNO_3$, means "mix 98 parts by weight of hydric sulphate with 101 parts by weight of potassic nitrate," and if we appended the expression $- HNO_3$, we should thereby add "take away 63 parts by weight of hydric nitrate." I do not think that the signs + and − should ever be used in any other sense than this. With regard to the arrangement which may be given to the elements of a formula, in order to explain any particular reaction of a compound, I hold that the utmost liberty should prevail, to vary such arrangements, in accordance with the convenience of each particular reaction. Thus urea may be written, in the hydrochloric acid type, as $(NH_4)(CNO)$, in the water type, as  $\genfrac{}{}{0pt}{}{CN}{NH_4}O$, in the diammonia type, as  $\overset{CO}{\underset{H_2}{H_2N_2}}$, or in the marsh-gas type as  $\overset{NH_2}{\underset{O}{NH_2C}}$

The only symbols which I make use of beyond those of elements numbered, in building up a formula for any particular reaction, are brackets, enclosing the symbols of a group of elements; and by thus dividing off the symbols of some constituents of a molecule from the remainder, I mean simply to request my reader to look upon the elements thus bound together, as behaving like one another in the reaction under consideration.

Thus in the formula $Ag(NO_3) + KCl = AgCl + K(NO_3)$, the brackets mean that in this reaction we have not to consider any separation of oxygen and nitrogen, but a separation of the group $NO_3$ from silver, and a combination of this group with potassium. Some formulæ of organic bodies could not be distinguished from one another without the use of brackets, or some equivalent grouping of the symbols. Thus vinic formate may be written $(C_2H_5)(C_2HO_2)$, or  $\begin{matrix}C_2H_5\\CHO\end{matrix}O$ indifferently, while methylic acetate would be $(CH_3)(C_2H_3O_2)$ or  $\begin{matrix}CH_3\\C_2H_3O\end{matrix}O$.

There is one serious deficiency in our present mode of representing compounds, a deficiency which will doubtless be supplied at a future time. We do not in any way represent the energy of each element by its symbol, nor the alterations which that energy undergoes when the element enters into any particular combination. Thus O represents 16 parts by weight of oxygen just as much in the free molecule $O_2$ as in combination with hydrogen as water, or with less hydrogen in hydric peroxide, or with nitrogen in nitrous acid, in each of which compounds its active forces, as judged of by its reactions, are entirely different from those which it manifests in the others. It is probable that the first step towards supplying this great want may be provided by determinations of the total heat of elements and compounds, *i.e.*, the sum of the specific heat from the absolute zero. The formula of every compound should describe how much less total heat its elements have than in the free state.

The term "volume" is now by common consent used to denote the volume of 16 parts by weight of oxygen. I have for some years past given an absolute measurement of the volume, which is found exceedingly convenient by learners, and useful for calculations. My absolute volume is 11·19 litres; but for most purposes it is taken at 11·2; which is the bulk of 16 grammes of oxygen at 0°C. and 760 millimetres. With the aid of this number, and the molecular weights of volatile bodies, it is easy to calculate the bulk of any given weight in practical problems.

# PROCEEDINGS

AT THE

# MEETINGS OF THE CHEMICAL SOCIETY

## January 21st, 1861.

Dr. Williamson, F.R.S., President, in the Chair.

The following were elected Fellows of the Society:—

**Ramsay Morton**, Esq., University Hall, Gordon-square; **John Penticost**, Esq., 1, Park-street, Torquay.

The following papers were read:—

"On Urochrome, the Colouring Matter of Urine:" by Dr. **Thudichum**.

"On the Absorption of Mixed Gases in Water:" by W. M. **Watts**.

"Remarks on Ground Ice:" by **Richard Adie**.

## February 4th, 1861.

Dr. **Frankland**, F.R.S., Foreign Secretary, in the Chair.

The following were elected Fellows of the Society:—

J. **Wrightson**, Esq., M. **Antonio Alves de Ferrara**, **Charles Lambert**, Esq.

The following paper was read:—

"On Mordenite, a mineral from the Trap of Nova Scotia:" by Dr. **How**.

### February 18th, 1864.

Dr. Williamson, President, in the Chair.

The following were elected Fellows of the Society:—

Anselm Odling, Esq., Nine Elms, Vauxhall; Benjamin E. R. Newlands, Esq., 19, West-square, Southwark; Henry Bassett, Esq., 36, Ampthill-square; Dr. Campbell Morfitt, Paris; Alfred Henry Allen, Esq., School of Practical Science, Sheffield; M. Sidney Gibbons, Esq., 5, Collens-street East, Melbourne; Thomas Stevenson, Esq., M.B., Guy's Hospital; James Dearden, Esq., Great Harwood, near Accrington.

The following papers were read:—

"On Acetanilide:" by C. Greville Williams.

"On the Conversion of Monocarbon-acids into the corresponding Dicarbon-acids:" by Prof. Kolbe.

"On a new formation of Malonic and Succinic Acids:" by Dr. Hugo Müller.

"On a new class of Sulphuretted Organic Compounds:" by Baron von Oefele.

A verbal communication was made by Dr. Hofmann on some experiments made by M. George Ville on the varying absorption of nitrogen by plants.

---

### March 3rd, 1864.

Dr. Williamson, President, in the Chair.

The following were elected Fellows of the Society:—

Edward Baines, Esq., Toronto, Canada West; William Ritchie, junr., Esq.

The following papers were read:—

"On the Non-metallic Impurities of Refined Copper:" by Prof. F. A. Abel.

"On the Synthesis of Leucic Acid:" by Dr. Frankland, F.R.S.

## March 17th, 1864.

Dr. **Williamson**, President, in the Chair.

The following were elected Fellows of the Society:—

**Thomas G. Bell**, Esq.; **Benjamin C. Staples**, Esq.

The following paper was read:—

"On Nitro-compounds:" by **Edmund J. Mills**.

---

## Anniversary Meeting, March 31st, 1864.

Dr. **Williamson**, President, in the Chair.

The following report was read by the President:—

Gentlemen,

It is my pleasing duty to report to you that, during the year just expired, the Chemical Society has continued to increase in the number of its members, and to show other signs of flourishing vitality. We now number 426 fellows, 35 foreign members, and 7 associates. 39 Fellows have been elected into the Society since the last anniversary meeting, whilst 2 former Fellows have resigned. We have to deplore the death of 3 Fellows, viz., Mr. **Conington**, Mr. **Stark**, and the Rev. Wm. **Walton**.

From among our foreign members we have lost two of the fathers of chemistry, **Rose** and **Mitscherlich**.

**Francis Thirkill Conington**, third son of the Rev. **Richard Conington**, was born January 3rd, 1828, at Boston, where his father was incumbent of a chapel of ease. After having been sent to two previous schools, he finally went to Rugby at the beginning of 1842, and remained there till October 1846. He was educated chiefly under Dr. **Tait**, who became head-master in the summer of 1842. His house-master and tutor was the Rev. **Charles Mayor**, who died just as he was leaving the school. In October 1846 he began residence at Corpus Christi College, Oxford, where he had obtained a Lincolnshire scholarship in the previous June. In the Easter examination of 1850, he obtained a second class in classics, having shortly before succeeded to a fellowship at his college. In 1851, and the next year, he spent some time abroad as a travelling tutor. In the middle of 1853 he was appointed Vice-Principal and Chief Classical Master of the Pulteney College, then newly established at Bath—an appointment which he resigned in the summer of 1855. From that time he resided in London. For two years he studied chemistry in the laboratory of University College, and subsequently gave me the benefit of his assistance in some researches in which I was engaged. He then published his "Handbook of Chemical Analysis," which supplied the want of an elementary text-book for laboratory students on the system of Gerhardt's atomic weights.

Mr. Conington subsequently wrote several valuable original articles in Watts's Dictionary of Chemistry, especially those on Inorganic Analysis, and on the Benzoyl Series.

An article on Owen's Palæontology, in Fraser's Magazine, is also attributed to him. His activity was however not confined to the domain of physical science; for he was, during several years, an active contributor to several Journals and Reviews.

For some time he discharged the duties of Examiner in the School of Natural Science at Oxford, and it was during one of these examinations, that the first serious symptoms of pulmonary disease showed themselves in him. He died on the 20th November, 1863. An earnest and enlightened man, such as there are but too few.

William Stark was born in the City of Norwich, January 3rd, 1788. He pursued science in very early life, and at the age of 13 conducted a course of chemical experiments, with his friend and schoolfellow, Mr. Philip Taylor, with whom he kept up a friendly intercourse, which terminated only in death. Mr. Stark was devotedly attached to the study of medicine and surgery, and acquired considerable theoretical knowledge of these subjects, which would, by choice, have been his pursuit in life, had not circumstances directed his talents into another channel. In recording the demise of this gentleman, it is but justice to his memory to give a slight sketch of the rise and progressive development of one important branch of the trade of his native city, to which he very largely contributed. About the year 1800 Mr. Stark was associated with Lieutenant-Colonel Harvey in the prosecution of designs for Fillover weaving in the shawl trade. This led to the gradually increasing manufacture of those beautiful fabrics made by Mr. J. F. Smith, the brother of Sir E. Smith, vice-president of the Linnæan Society, and Mr. Thomas Paul; and for which Norwich became so justly celebrated. About the year 1806 Mr. Stark joined Messrs. Sims and Pitchford, at that time conducting the first and only chemical laboratory in Norwich. Here he commenced a branch of chemical dyeing for the purpose of establishing certain *permanent* colours upon cotton fabrics. This business was successfully carried on for about five years, when cheaper methods of dyeing were resorted to, and it no longer answered the purpose of Messrs. Sims and Co. to continue the business; but this was the origin of the superiority of Norwich Fillovers, and made them stand so deservedly high in the market. It is stated that the process of dyeing *permanently* upon *cotton* the three principal colours, *i.e.* scarlet, crimson, and pink, remains undisclosed to the present time. Mr. Stark was elected a Fellow of the Geological Society of London in the year 1838, and a Fellow of the Chemical Society in 1843. He was also a member of the Norwich Philosophical Society, under the Presidency of Dr. Rigby, and read, in his turn, several papers upon subjects in natural and experimental philosophy. He was the author of other scientific papers published in "The Annals of Philosophy," "The Philosophical Magazine," &c. Mr. Stark wrote an article in reply to Sir Charles Lyell, upon "The Formation of Sand Pipes in Chalk Pits," which gave rise to an animated discussion at a meeting of the Geological Society of London. He was employed in the analyses of some poisoned stomachs in the years 1816 and 1829, and the Judges of Assize complimented Mr. Stark upon the precision of his statements, and the general clearness of his evidence. Mr. Stark was intimately acquainted with many of the scientific men of his day, and his correspondence with them contained some valuable facts in chemistry and other branches of science, which are said to have led to important practical results. The last three years of his active and useful life were overshadowed by the loss of sight. He brought up twelve children all of whom, except one, arrived at adult age. He has passed away beloved and esteemed by all who knew his worth.

Heinrich Rose was born in the year 1795 at Berlin, where his father, Valentine Rose, the son of Valentin Rose the elder, the discoverer of Rose's fusible metal, was apothecary and assessor at the Ober-Collegium-Medicum. Henrich Rose also applied himself at first to the study of pharmacy at Dantzic, where he lived through the terrible siege of that city under Rapp, and nearly fell a victim to typhus fever. In the war of 1815, he and his three brothers took an active part. After peace was concluded he pursued his studies at Berlin; in 1819 he went to Stockholm to study under Berzelius; in 1821 he took his Doctor's degree at Kiel; and in 1822 he went to Berlin, where he was elected Extraordinary Professor of Chemistry in 1823, and Ordinary Professor in 1835. In that university he continued to work, without intermission, by the side of his brother, the distinguished mineralogist, Gustav Rose. Though he never sought for external honours, they were bestowed upon him in abundance; it may be sufficient here to particularise the order, "pour le Merite" of the civil class.

The precept and example of his great teacher, Berzelius, for whom he always manifested the greatest love and reverence, determined the whole course of his scientific life. The great powers of his mind were concentrated upon Inorganic, and especially upon Analytical Chemistry. On this field of research he stands unrivalled. The fact that, in the entire series of "Poggendorff's Annalen," extending to more than a hundred volumes, there is scarcely one that does not contain a paper by Heinrich Rose, is sufficient to show that his whole life was one continued manifestation of intellectual activity.

Among the numerous important results of his analytical investigations, may be especially mentioned the discovery, or rather re-discovery of the metal *Niobium*. The history of this metal is remarkable. It was originally obtained in 1801, by Hatchett, from columbite, a black mineral from Massachusetts, and thence called *Columbium*. Wollaston, in 1809, examined it further, and pronounced it to be identical with tantalum, a metal discovered by Ekeberg in Swedish tantalite. This idea of the identity of the two metals remained current till 1846, when Rose, by a more careful investigation, was led to conclude, that the American columbite, and likewise the tantalite of Bodenmais in Bavaria, contained two acids bearing a close resemblance to tantalic acid, but nevertheless distinct from it, and containing two different metals, to which he gave the names *Niobium* and *Pelopium*. But by a later investigation, he found that these two acids really contain the same metal associated with different quantities of oxygen. This metal, contained in American columbite and Bavarian tantalite, is evidently identical with the columbium, discovered more than sixty years ago by **Hatchett**; but as the rediscovery of it is certainly due to **Rose**, who has moreover completed its chemical history by the preparation and exact analysis of a large number of its compounds, chemists are, for the most part, agreed to designate it by the name which he assigned to it, namely, *Niobium*.

Other researches of **Rose** more particularly deserving of notice, are those on phosphoretted hydrogen, on the compounds of sulphur with chlorine, bromine, and iodine, on the anhydrous salts of ammonia, on chlorosulphuric acid, and an important series of experiments published in the years 1851, 1856, on the influence of water in chemical reactions.

The results of Rose's analytical investigations are collected together in his "Handbook of Analytical Chemistry," the sixth edition of which was published, as an original French edition, at Paris, in 1861. To form an idea of the amount of labour expended on this great work, it is necessary to bear in mind, that every statement is based upon, or confirmed by, an experiment, and in many cases of a series of experiments, made by the author himself. In the last year of his life he was at work upon an Elementary Treatise on Analytical Chemistry (*Lehrbuch der Analytischen Chemie*), for which also a large number of new experiments were made in his laboratory.

It was thus that, with advancing years, the activity and industry of this extraordinary man continued unabated. A year before his death he said, "I have at most a few years to live, and there is still so much work to be done." In his latter years, he scarcely allowed himself an hour's recreation during the day; only late in the evening, in all weathers and at all seasons, he would take a long walk, and even then his mind was busily engaged upon the properties of bodies and the discovery of new methods of analysis.

While respected by all, he inspired those who had the happiness of knowing him intimately, with a life-long feeling of affectionate regard. He had borne arms for the liberation of his country, and always retained for it a warm and patriotic affection. In his domestic circle, he suffered much affliction, having lost two wives and his only child; his third wife and an only grandchild survive him. But he never allowed his private griefs to interfere long with the discharge of his duties; indeed it was wonderful to see how from a depth of sorrow, amounting almost to despair, he would rouse and brace himself up to the work of teaching and investigation. Work was indeed to him a never-failing source of consolation.

The close of his life was easy. He kept his bed for only four days, and a week before his death he taught with undiminished energy. Even on his dying day he asked for writing materials, and a proof-sheet of his book for correction, and assured those around him that he felt well and able to get up. He died on the 27th of January, 1864, at noon, being carried off by inflammation of the lungs.

Eilhardt Mitscherlich was born on the 7th of January, 1794, at Neuende, near Jever, in Oldenburg, where his father was preacher. He received his first scientific instruction at the gymnasium of Jever, and afterwards followed his teacher, the celebrated historian Schlossler, who looked after his education with the kindest solicitude, to Frankfort. In 1811, he went to Heidelberg, where he devoted himself to history and philology, especially that of the oriental languages. In addition to these historical and philological studies, Mitscherlich likewise devoted himself to mineralogy and geology, medicine, physics, and chemistry, chiefly with the view of preparing himself for an extended scientific journey in the East, which was at that time one of his most cherished objects. But the natural sciences had so strong an attraction for him, that he soon gave himself up entirely to them, and especially to chemistry.

His efforts in this direction were soon crowned with the most brilliant success. In the year 1818, he discovered that, to every artificially crystallised phosphate, there corresponds an arsenate of similar crystalline form and chemical composition. This discovery led him to researches on the connection between the crystalline form and chemical constitution of compounds in general; and as the final result of a laborious series of investigations, he announced the law of Isomorphism,—a discovery which has always been considered to reflect the greatest honour on his name. The recognition of his contemporaries also was not wanting. Berzelius entered with him into a scientific correspondence, which, when Mitscherlich, in 1819—1821, worked with him at Stockholm, soon ripened into a cordial friendship. The Royal Society of London conferred upon Mitscherlich the Copley Medal; the Academy of Sciences, at Berlin, elected him a member in 1821, and he was at the same time appointed to the Ordinary Professorship of Chemistry in the University of Berlin, which, till then, had been held by Klaproth. From that time till his death, Mitscherlich continued his labours uninterruptedly in Berlin.

Among the numerous scientific researches which he published in "Poggendorff's Annalen," I have next to notice a series of investigations by which he succeeded in producing artificially a large number of natural minerals formed at high temperatures, namely, by fusing their constituents together in the required proportions, the artificial minerals thus obtained resembling the natural minerals in form and physical properties. He was led to this inquiry by observing that the slags obtained in the smelting of copper ores at Fahlun, in Sweden, crystallised on cooling, partly in the form of olivin, partly in that of augite.

Highly interesting results of another kind were obtained by his observations on the expansion of crystals by heat. By measuring the angles of crystals at different temperatures with a highly improved reflecting goniometer, he was enabled to show that all crystals not belonging to the regular system, expand unequally in different directions—an observation of the highest importance to molecular physics. His discovery of the allotropy of sulphur was also of great importance, and that of the formation of benzole by the destructive distillation of a benzoate mixed with an alkaline hydrate, has been particularly valuable. In addition to these discoveries must also be mentioned a large number of researches in analytical and organic chemistry. Some of his researches were published in scientific journals, while others are contained in his "Lehrbuch der Chemie."

This work is distinguished by a systematic arrangement of the matter well adapted to the purposes of instruction, and by a remarkably lucid and attractive style. It is unfortunate that the author was prevented, for the last sixteen years, by other scientific labours, and by professional duties which took up a large portion of his time, from undertaking the preparation of new editions suited to the advanced state of chemical science; nevertheless his "Lehrbuch" will always be valuable, and has already served as a model and groundwork for other works of the same kind.

In the latter years of his life, Mitscherlich was chiefly occupied with geological researches, on the extinct volcanoes of the Eifel and of the South of France. It is believed that these researches will shortly be published.

All **Mitscherlich's** labours were animated by a truly philosophical spirit. His researches were invariably directed to subjects of great interest; his discoveries have opened out new views, and broken ground for other inquirers. The great variety of his intellectual training imparted to his teaching a high significance and peculiar charm: his lectures were especially distinguished by the elegance of his experiments; and the care which he bestowed on them, was evidenced by the completeness and costliness of his private collections.

Foreign distinctions were abundantly bestowed on **Mitscherlich**. He was a member of numerous Academies. Among the large number of his Orders, we must especially mention the "Ordre pour le mérite." In his capacity of director of pharmaceutical studies, and of member of the Medical College, he bore tho title of "Geheim-Ober-Medicinal-Rath."

His life was in every respect most happy. It was only in his last years that he suffered from illness, and this was made lighter to him by the affectionate care of his wife. He was removed from the circle of his friends by an easy death on the 28th of August, 1863.

**Mitscherlich** was in friendly relation with a large number of distinguished men. By his pupils, he was highly venerated and sincerely beloved: for, the amiable and benevolent disposition which shone forth in all his actions, won the hearts of all who had the good fortune to know him; and as the history of science will preserve his name for ever, so also will the remembrance of his character continue to live in many thankful hearts.

---

List of Papers read at the Meetings of the Chemical Society, from March 30, 1863, to March 30, 1864:—

1. "Contributions to the History of the Tolyl Series:" by **Eugene Sell**, of Bonn.
2. "On some Derivatives of Naphthylamine:" by Messrs. **Perkin** and **Church**.
3. "On Vanadium Ochre:" by Dr. **Phipson**.
4. "On the Chloromaleic Acid obtained from Tartaric Acid:" by **W. H. Perkin**.
5. "On Pickeringite:" by Dr. **How**.

6. "On the Derivatives of Hydride of Heptyl:" by C. Schorlemmer.
7. "On the Hexyl Group:" by Wanklyn and Erlenmeyer.
8. "On a Curious Instance of Electrolytic Action:" by Prof. Abel.
9. "Note on some Metamorphoses of Oxalic Acid:" by Arthur H. Church, B.A.
10. "Note on the Quantitative Determination of Phosphoric Acid by Salts of Magnesia:" by Robert Warington, Jun.
11. "On the Synthesis of Certain Series of Organic Compounds:" by Mr. Carlton, B.A.
12. "On the Iodide of Iodammonium:" by Prof. F. Guthrie.
13. "On the Detection of Nitric Acid:" by Dr. Sprengel.
14. "On the Variations of Hippuric Acid in Human Urine:" by Dr. Thudichum.
15. "On Azulene:" by S. Piesse.
16. "On the Occurrence of Vanadium in English Pig-iron:" by E. Riley.
17. "On a New Method of Producing the Mercury-Compounds of the Alcohol-Radicles:" by Drs. Frankland and Duppa.
18. "On a new form of Sulphuretted Hydrogen Apparatus:" by Dr. Phipson.
19. "On the Chemical Constitution of the so-called Alcohol-Radicles:" by C. Schorlemmer.
20. "Note on the Quantitative Determination of Sulphur:" by Dr. D. S. Price.
21. "On Essential Oils:" by Dr. Gladstone.
22. "On a New Reaction for the Production of the Zinc-Compounds of the Alcohol-Radicles:" by Drs. Frankland and Duppa.
23. "On a New Form of Gas-combustion Furnace for Organic Analysis:" by W. Herapath.
24. "On Urochrome, the Colouring Matter of Urine:" by Dr. Thudichum.
25. "On the Absorption of Mixed Gases in Water:" by W. M. Watts.
26. "On Mordenite, a Mineral from the Trap of Nova Scotia:" by Dr. How.
27. "On Acetanilide:" by C. Greville Williams.
28. "On the Conversion of Monocarbon-acids into the corresponding Dicarbon-acids:" by Prof. Kolbe.

29. "On a new formation of Malonic and Succinic acids:" by Dr. Hugo Müller.
30. "On a New Class of Sulphuretted Organic Compounds:" by Baron von Oefele.
31. On the Non-Metallic Impurities of Refined Copper:" by Prof. F. A. Abel.
32. "On the Synthesis of Leucic Acid:" by Dr. Frankland.
33. On Nitro-compounds:" by Mr. E. J. Mills.

List of Discourses delivered at the Meetings of the Chemica Society, between March 30th, 1863, and March 30th, 1864:—

1. "On the Constitution of Salts:" by Dr. Lyon Playfair.
2. "On the Effects of Intense Heat on Fluids:" by W. R. Grove, Q.C.
3. "On Synthetic Methods in Organic Chemistry;" by Prof. Berthelot.

---

The following gentlemen were elected as Council and Officers for the ensuing year:—

*President.*—Alexander W. Williamson, Ph.D., F.R.S.

*Vice-Presidents who have filled the Office of President.*—W. T. Brande, F R.S., Sir B. C. Brodie, F.R.S., C. G. B. Daubeny, M.D., F.R.S., Thomas Graham, F.R.S., A. W. Hofmann, L.L.D., F.R.S., W. A. Miller, M.D., F.R.S., Lyon Playfair, Ph.D., C.B., F.R.S., Colonel Philip Yorke, F.R.S.

*Vice-Presidents.* — Walter Crum, F.R.S., Alfred Smee, F.R.S., John Stenhouse, LL.D., F.R.S., Robert Warington, F.R.S.

*Secretaries.*—Theophilus Redwood, Ph.D., William Odling, M.B., F.R.S.

*Foreign Secretary.*—E. Frankland, Ph.D., F.R.S.

*Treasurer.*—Warren De la Rue, Ph.D., F.R.S.

*Other Members of the Council.*—F. A. Abel, F.R.S., Thomas Andrews, M.D., F.R.S., Dugald Campbell, H. Debus, Ph.D., F.R.S., J. B. Lawes, F.R.S., A. Matthiessen, Ph.D., F.R.S., Hugo Müller, Ph.D., E. C. Nicholson, W. J. Russell, Ph.D., Maxwell Simpson, M.B., F.R.S., J. T. Way, C. Greville Williams, F.R.S.

*Librarian.*—Henry Watts, B.A., F.C.S.

*Collector.*—Mr. Thomas West, Burlington House.

The thanks of the meeting were voted to the President, Officers, and Council for their services to the Society during the past year

## THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY.

**Drs.**

| | | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|---|
| 1863-4. March 25. | To Balance on hand | | | | 519 | 14 | 7 |
| | ,, Yearly Dividend on £800 3 per cent Consols, less Income-tax | | | | 23 | 6 | 0 |
| | ,, Sale of Journals | | | | 48 | 2 | 4 |
| | ,, Sundry Receipts from March 25th, 1863, to March 23rd, 1864, as below:— | | | | | | |
| | Life Compositions | 100 | 0 | 0 | | | |
| | Admission Fees | 72 | 0 | 0 | | | |
| | Resident Members' Subscriptions previous to 1863 | 14 | 0 | 0 | | | |
| | Non-resident Members' Subscriptions previous to 1863 | 7 | 0 | 0 | | | |
| | Resident Members' Subscriptions for 1863 | 88 | 0 | 0 | | | |
| | Non-resident Members' Subscriptions for 1863 | 29 | 0 | 0 | | | |
| | Resident Members' Subscriptions for 1864 | 346 | 0 | 0 | | | |
| | Non-resident Members' Subscriptions for 1864 | 90 | 0 | 0 | | | |
| | | | | | 746 | 0 | 0 |
| | | | | | £ 1337 | 2 | 11 |

**Crs.**

| | | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|---|
| 1863-4 Journal. | By Editor's Salary to 25th March, 1864 | 95 | 0 | 0 | | | |
| | ,, Printing Journal | 207 | 11 | 9 | | | |
| | ,, Distributing Journal | 26 | 17 | 2 | | | |
| | ,, Translating (Mr. Watts) | 2 | 16 | 0 | | | |
| | | | | | 342 | 4 | 11 |
| Proceedings of Royal Society. | ,, Annual Subscription to Royal Society for their Proceedings sent to the Fellows of the Chemical Society | 50 | 0 | 0 | | | |
| | | | | | 50 | 0 | 0 |
| Library. | ,, Librarian's Salary to 25th March, 1864 | 25 | 0 | 0 | | | |
| | ,, Books and Magazines | 48 | 15 | 8 | | | |
| | ,, Subscription to Cavendish Society | 1 | 1 | 0 | | | |
| | ,, Bookbinding | 13 | 1 | 3 | | | |
| | | | | | 87 | 17 | 11 |
| Collector and Clerk. | ,, Collector's Commission | 37 | 6 | 0 | | | |
| | ,, Clerk | 3 | 0 | 0 | | | |
| | | | | | 40 | 6 | 0 |
| General Printing Stationery, &c. | ,, Harrison & Sons' account | 6 | 10 | 0 | | | |
| | ,, Receipt Book | 1 | 12 | 0 | | | |
| | ,, Postage Envelopes | 5 | 12 | 6 | | | |
| | ,, Stamps | 4 | 2 | 10 | | | |
| | | | | | 17 | 17 | 4 |
| House Expenses. | ,, Royal Society, Share of Tea Expenses | 14 | 6 | 4 | | | |
| | ,, ,, Share of Illuminations | 6 | 0 | 0 | | | |
| | ,, T. Hux, 1 year's Salary to 25th March, 1864 | 20 | 0 | 0 | | | |
| | ,, ,, Gas account | 3 | 9 | 3 | | | |
| | ,, ,, Petty Expenses | 1 | 17 | 9 | | | |
| | ,, W. Page, Cleaning | 1 | 1 | 0 | | | |
| | ,, Gate Porter | 2 | 2 | 0 | | | |
| | ,, Snowdon & Sons, Repairs | 2 | 6 | 0 | | | |
| | | | | | 51 | 2 | 4 |
| | ,, Illustration of Berthelot's Lecture | 2 | 2 | 0 | | | |
| | | | | | 2 | 2 | 0 |
| Furniture. | ,, Snowdon & Sons, Book Case | 24 | 10 | 0 | | | |
| | | | | | 24 | 10 | 0 |
| 1864. March 4. | ,, Purchase of £100 Consols | 91 | 7 | 6 | | | |
| | | | | | 91 | 7 | 6 |
| | ,, Balance at Messrs Coutts | | | | 629 | 14 | 11 |
| | | £ | | | 1337 | 2 | 11 |

**Assets.**

| | £ | s. | d. |
|---|---|---|---|
| Balance at Messrs Coutts | 629 | 14 | 11 |
| Invested in 3 per cent Consols | 900 | 0 | 0 |
| | £1529 | 14 | 11 |

Examined and found correct,

EDWARD ASH HADOW, } *Auditors.*
E. CHAMBERS NICHOLSON. }

London. March 23rd, 1864.

### April 7th, 1864.

Dr. Williamson, President, in the Chair.

Wentworth Lascelles Scott, Esq., was elected a Fellow of the Society.

The following papers were read:—

"On Oxaniline:" by Dr. R. Schmidt.

"On the Tetrabasic or Orthocarbonate of Ethyl:" by Henry Bassett.

---

### April 21st, 1864.

Dr. Williamson, President, in the Chair.

The following were elected Fellows of the Society:—

James Maclean, Esq., 67, Buchanan-street, Glasgow; George Ward, Esq., Leeds; John Dowling, Esq., 2, Upper Buckingham-street, Dublin.

The following were elected Foreign Members of the Society:—

M. Dessaignes, M. Erdmann, Von Fehling.

The following papers were read:—

"On the Hexyl Group." by Prof. Wanklyn and Dr. Erlenmeyer.

"On an Alkaloid obtained from the Seeds of *Ricinus Communis*:" by R. V. Tuson.

"On the Action of Hydrobromic Acid and of Hydriodic Acid upon Polyatomic Acids, and on the behaviour of Iodo-substitution Compounds towards Hydriodic Acid:" by Prof. Kekulé.

---

### May 5th, 1864.

Dr. Williamson, President, in the Chair.

The following were elected Fellows of the Society:—

Edward Henry Prentice, Stowmarket, Suffolk; Carl

Schorlemmer, Owens College, Manchester; Edward Frederick Teschemacher, 1, Highbury-park North; T. S. Conisbee, Herbert's-buildings, Waterloo-road, S.

Sir Benjamin Brodie delivered a discourse "On the Organic Peroxides, theoretically considered."

---

## May 19th, 1864.

Dr. Williamson, President, in the Chair.

The following were elected Fellows of the Society:—

Dr. Wrightson, Birmingham; Manning Prentice, Esq., University College.

The following papers were read:—

"On the Constitution of Wood-spirit:" by William Dancer.

"On the Chlorophosphide of Nitrogen, and on two new acids related thereto:" by J. H. Gladstone and J. D. Holmes.

"On a new method of Gas Analysis:" by Drs. Williamson and Russell.

"On the Classification of the Elements according to their Atomic Weights." by Professor Williamson.

## June 2nd, 1864.

Dr. Williamson, President, in the Chair.

The following was elected a Fellow of the Society:—

Charles Tomlinson, Esq., Lecturer on Science at King's College.

Professor G. G. Stokes, delivered a discourse "On the Detection and Discrimination of Organic Bodies by means of their Optical Properties."

---

## June 16th, 1864.

Dr. Williamson, President, in the Chair.

The following were elected Fellows of the Society:—

Sydney Pontifex, Esq., 106, Leadenhall-street; G. W.

Knox, Esq., Northern Chemical Works, Bristol; Michael Carteighe, Esq., 172, New Bond Street.

The following papers were read:—

"On the Identity of Methyl and Hydride of Ethyl:" by C. Schorlemmer.

"On the Action of Baryta upon Suberic and Azelaic Acids:" by R. T. Dale.

Dr. Sprengel gave an account of an instrument for producing a vacuum.

June 30th, 1864.

Dr. Williamson, President, in the Chair.

John Thomas Way, Esq., delivered a discourse "On the Philosophy of English Agriculture."

November 3rd, 1864.

Dr. Williamson, President, in the Chair.

The following papers were read:—

"On the Isolation of the Electro-negative Radicle Valeryl:" by Professor Wanklyn.

"On the Existence of Nitrogen in Steel:" by Messrs Stuart and Baker.

"On the Concentration of Nickel in Lead:" by W. Baker.

"On the Blue Colouring Matter of Forest Marble:" by Professor Church.

"On the Effect of Ignition on Garnets, &c:" by Professor Church.

November 17th.

Dr. Williamson, President, in the Chair.

The following papers were read: –

"On the Brine of Salted Meat:" by Dr. Marcet.

"On the Nature of Compound Ethers:" by Professor Wanklyn.

## December 1st, 1864.

Dr. Williamson, President, in the chair.

The following were elected Fellows of the Society:—

Lieutenant Clayton S. Beauchamp, Royal Engineers; John Bray, Esq., High-street, Sheerness; Charles Ekin, Esq., Bath; Henry Heywood, Esq., Broomhall Park, Sheffield; Lieutenant H. M. Hozier, 2nd Life Guards, New-street, Spring Gardens; Daniel Harmer Jay, Esq., Frog Island, Leicester; W. W. Rouch, Esq., Norfolk-street, Strand; Joseph F. Paine, Esq., M.A., Magdalen College, Oxford; J. G. F. Richardson, Esq., Manufacturing Chemist, Leicester; Lieutenant-Colonel H. Y. D. Scott, Royal Engineers, South Kensington Museum; J. Berger Spence, Esq., Newton Heath, near Manchester; Hermann Sprengel, Esq., Ph.D., Chemical Works, Kennington Common; Alfred Pythian Turner, Esq., 3, Upper Baker-street.

The following names were removed from the List of Fellows:—

Alfred Binyon, W. T. Doyne, John Jones, Robert Railton, J. H. Robson, R. S. Roper, Richard Taylor, C. W. Swaisland, D. W. B. M$^c$Kinley.

The following papers were read:—

"On the Distribution of Albumen through Muscular Tissue:" by Dr. Marcet.

"On the Action of Sulph-hydrate of Potassium upon Acetic Ether:" by Professor Wanklyn.

"On the Density of certain Minerals:" by Professor A. H. Church.

## December 15th, 1864.

The following gentleman was elected a Fellow of the Society:—

Alexander Y. Stewart, Apothecaries' Hall.

The following papers were read:—

"On the Action of Ammonia on Sulphochloride of Phosphorus:" by Dr. J. H. Gladstone, and J. D. Holmes, Esq.

"Remarks On Chemical Nomenclature and Notation:" by Professor Williamson.

## Donations to the Library in the year 1864.

"A Dictionary of Chemistry and the Allied Branches of other Sciences:" by Henry Watts: Parts XI–XXII: from Messrs. Longman and Co.

"The Relations of Science to Modern Civilization:" by Prof. Hennessy: from the Author.

"On some Effects produced by a Fluid in Motion:" by G. F. Rodwell: from the Author.

"On the Supposed Deterioration of the Soil of Great Britain:" by Dr. Daubeny: from the Author.

"Researches on the Refraction, Dispersion and Sensitiveness of Liquids:" by Dr. J. H. Gladstone and the Rev. T. P. Dale: from the Authors.

"Researches on the Solar Spectrum and on the Spectra of the Chemical Elements:" by G. Kirchhoff: Part II: Translated by Dr. H. E. Roscoe: from the Translator.

"Tables of Chemical Formulæ:" arranged by William Odling: from the Author.

"On the Physical Cause of the Glacial Epoch:" by E. Frankland: from the Author.

"An Inquiry into the Physiological and Medicinal Properties of the *Veratrum viride*:" by Samuel R. Percy, M.D.: from the Author.

"Elements of Chemistry, Theoretical and Practical:" by William Allen Miller: Part II, Inorganic Chemistry, 3rd edition: from the Author.

"Report of Experiments on the Growth of Wheat for twenty years in succession on the same Land:" by J. B. Lawes and J. H. Gilbert: from the Authors.

"Further Report of Experiments with different Manures on Permanent Meadow Land:" by J. B. Lawes and J. H. Gilbert: from the Authors.

"On the Chemistry of the Feeding of Animals for the Production of Meat and Manure:" by J. B. Lawes: from the Author.

"Leçons de Chimie et de Physique, professées à la Société Chimqiue de Paris, en 1862 et 1863:" from the Society.

"Leçons sur les Méthodes générales de Synthèse en Chimie Organique:" from M. Berthelot: from the Author.

"Matériaux pour servir à l'histoire de la Cérite et du Gadolinite:" par M. Delafontaine: from the Author.

"Recherches sur les Acides Silico-tungstiques:" par C. Marignac: from the Author.

"Leçons de Philosophie Chimique:" par A. Wurtz: from the Author.

"Mémoire sur les Glycols ou Alcools Diatomiques:" par A. Wurtz: from the Author.

"Recherches sur les Affinités:" par MM. Berthelot et Péan de St. Gilles: from the Authors.

"Vichy et ses Environs:" par L. Piesse: from the Author.

"Libros del Saber de Astronomia del Re Don Alfonso de Castilla, compilados, anotados y comentados: por Don Manuel Rico y Sinobras:" Tomos I, II: from the Royal Academy of Sciences at Madrid.

"Ueber pharmaco-dynamischen Aequivalente für die wichtigsten Bestandtheile der Mineral-wasser:" von Dr. P. Phœbus: from the Author.

"Ueber die Delondre-Bouchardatschen Chinarinden:" von Dr. P. Phœbus: from the Author.

Periodicals:—

"Memoirs of the Royal Astronomical Society:" Vol. XXXII: (1862–63).

"Monthly Notices of the same," from January to December, 1864. from the Society.

"Quarterly Journal of the Geological Society for 1864:" from the Society.

"Proceedings of the Royal Institution of Great Britain," Vol. IV.

"List of Members, Officers, and Professors of the same for 1864:" from the Institution.

"The Mining and Smelting Magazine," January—December, 1864: from the Editor.

"Pharmaceutical Journal" for 1864: from the Editor.

"Chemical News," Nos. 209—262: from the Editor.

"Journal of the Society of Arts," Nos. 577–629: from the Society.

"Journal of the Photographic Society," January—December, 1864: from the Society.

"Annual Report of the Leeds Philosophical and Literary Society" (1862–63): from the Society.

"The London University Calendar" for 1864: from the University.

"The Scientific Record," Nos. 1 and 2: from the Editor.

"Annual Report of the Yorkshire Philosophical Society" for 1864: from the Society.

"Quarterly Journal of Science," Nos. 1—4: from the Editor.

"The Reader," Nos. 50–102: from the Editor.

"The Canadian Journal of Science and Arts," July, 1864: from the Canadian Institute.

"American Journal of Science and Art," from November, 1863—September, 1864: from the Editors.

"Journal of the Franklin Institute," Oct., 1863—Oct. 1864: from the Institute.

"Proceedings of the Academy of Natural Sciences at Philadelphia" (1863), Nos. 4—7: from the Academy.

"The Saint Louis Medical and Surgical Review:" edited by Dr. M. L. Linton, and Dr. F. M. White (new series), Nos. 1—4: from the Editors.

"Journal of the Argentine Pharmaceutical Society," Vols. I, II, III: from the Society.

"Les Mondes, Revue hebdomadère des Sciences:" par l'Abbé Moigno, Tome II, Liv. 16—Tome VI, Liv. 14: from the Editor.

"Bulletin de l'Académie des Sciences de St. Petersbourgh:" from the Academy.

"Bulletin des Séances de la Classe des Sciences de l'Académie Royale de Belgique" (1863): from the Academy.

"Annuaire de l'Académie Royale de Belgique" (1864): from the Academy.

"Memorie dell' Accademia delle Scienze dell' Istituto di Bologna," Serie 1, Tomo XII; Serie 2, Tomi I, II: from the Academy.

"Rendiconti delle Sessioni dell' Accademia delle Scienze dell' Istituto di Bologna," 1861–2 and 1862–3: from the Academy.

"Zeitschrift der Chemie und der Pharmacie," herausgegeben von Dr. E. Erlenmeyer, Bd. VII, Hefte 3—18: from the Editor.

"Jenaïsche Zeitschrift für Medicin und Naturwissenschaft; herausgegeben von der Medicinish-naturwissenschaftlichen Gesellschaft zu Jena," Band I, Heft 1: from the Society.

"Jahrbuch der königl-kaiserlichen geologischen Reichsanstalt zu Wien," Band XIII (April—December, 1863): from the Geological Institute of Vienna.

"Sitzungsberichte der königl-baeyrischen Akademie der Wissenschaften," 1863, Hefte 1—4; 1864, Bd. II, Heft 1: from the Academy.

"Öfversigt af Kongl. Vetenskaps Akademiens Förhandlingar," 1863: from the Royal Academy of Sciences at Stockholm.

"Oversigt over det Kongelige danske Videnskabernes Selskabs Forhandlinger, og dets MedlemmersArbeeten," (1862—63): from the Royal Danish Academy of Sciences.

# ERRATA.

| Page. | Line. | | | | |
|---|---|---|---|---|---|
| 258, | 7 from top, | *for* | $\rlap{-}C_8H_6\rlap{-}O_4$, | *read* | $\rlap{-}C_8H_{14}\rlap{-}O_4$. |
| 295, | 5 from bottom, | ,, | $MnO_2$, | ,, | $MnO_x$. |
| 296, | 22 from bottom, | ,, | V, | ,, | N. |
| 297, | 14 from bottom, | ,, | or, | ,, | so. |
| 299, | 6 from top, | ,, | moisture, | ,, | mixture. |
| 300, | 7 from top, | ,, | MnO 1·557, | ,, | $MnO_{1·557}$ |
| 300, | 10 from top, | ,, | 83·, | ,, | 8·3. |
| 300, | 15 from bottom, | ,, | 21·52, | ,, | 29·52. |
| 398, | 15 from top, | ,, | Separation, | ,, | Preparation. |

# INDEX.

A.

Abel, F. A., on the non-metallic impurities of refined copper, 164.
Absorption of chemical rays by reflection from polished surfaces, 76.
—— —— by transmission through gases, 72.
—— —— liquids, 71.
—— —— solids, 62.
—— —— vapours, 72.
—— of coloured rays, discrimination of organic substances by the, 305.
—— of mixed gases in water, on the: by W. M. Watts, 88.
Acetanilide, on: by C. Gr. Williams, 106.
Acetate of thallium, 149.
Acetic ether, on the action of sulphydrate of potassium, on: by J. A. Wanklyn, 418.
Acetyl, peroxide of, 272.
Acetylene, conversion of, into ethylene, 38.
—— formation of, by direct combination of carbon and hydrogen, 43.
Acid amidosalicylic, its conversion into oxaniline, 194.
—— azelaic, action of caustic baryta on, 261.
—— azophosphoric, 229, 234.
—— benzoic, action of chloride of iodine on, 332.
—— bromacetic, formation of, from glycollic acid, by the action of hydrobromic acid, 205.
—— bromopropionic, formation of, from lactic acid, by the action of hydrobromic acid, 205.
—— bromosuccinic, formation of, from malic acid, by the action of hydrobromic acid, 205.
—— carbonic, and water, formation of organic substances from, 40.
—— carbonic, and sulphurous acid, absorption of, in water, 98.
—— deutazophosphoric, 228, 231.
—— dichloracetic, on the preparation of, by Hugo Müller, 398.
Acid, glycollic, conversion of, into bromacetic acid by the action of hydrobromic acid, 205.
—— hippuric, researches on the physiological variations of the quantity of, in human urine: by J. L. W. Thudichum, 55.
—— hydriodic, on the action of, on polyatomic acids: by A. Kekulé, 209.
—— on the behaviour of iodo-substitution-compounds towards: by A. Kekulé, 206.
—— hydrobromic, on the action of, on polyatomic acids: by A. Kekulé, 203.
—— hydrochloric, electric spectra of metals in, 87.
—— hydrochloric, preparation of thallium from commercial, 119.
—— metastannic, liquid, 320.
—— malonic, on a new formation of: by Hugo Müller, 109.
—— molybdic, liquid, 326.
—— monochloracetic, on the preparation of: by Hugo Muller, 398.
—— pyrophosphamic, 237.
—— pyrophosphodiamic, 237.
—— silicic, on the properties of, and other analogous colloidal substances: by Thomas Graham, 38.
—— stannic, liquid, 32.
—— suberic, action of caustic baryta on, 260.
—— succinic, on a new formation of: by Hugo Muller, 109.
—— sulphurous, electric spectra of metals in, 86.
—— and carbonic acid, absorption of, in water, 98.
—— titanic, liquid, 325.
—— tungstic, liquid, 325.
Acids, on the conversion of monocarbonic, into dicarbonic acids: by H. Kolbe, 109.
—— organic, formation of, from aldehydes, 47.
—— —— on the peroxides of the radicles of the: by B. C. Brodie, 266.

Acids, polyatomic, on the action of hydrobromic, and of hydriodic acid on: by A. Kekulé, 203.
Air, analysis of, by Williamson and Russell's apparatus, 254.
—— and ammonia, absorption of, in water, 90.
"Al" root, the root of *Morinda citrifolia*, the best source of pure alizarin, 334.
Albumen, on the distribution of, through muscular tissue: by W. Marcet, 405.
Alcohol, formation of, from ethylene, 39.
—— methylic, synthesis of, 42.
Alcohol-radicles, on a new reaction for the production of the zinc-compounds of the: by E. Frankland and B. F. Duppa, 29.
Alcogel of silicic acid, 322.
Alcosol of silicic acid, 321.
Alizarin and purpurin, distinctive spectra of, 309.
Aldehydes, formation of, from alcohols, 47.
Alkali-metals, relations of thallium to the, 126.
Alkaloïd, note on an, contained in the seeds of the *Ricinis communis*, or castor-oil plant: by R. V. Tuson, 195.
Alloys, electric spectra of, 82.
Aluminium, its reflecting power for chemical rays, 77.
Aluminium and thallium, double sulphate of, 142.
Amidogens, 162.
Amido-nitrosogens, 162.
Ammonia and air, absorption of, in water, 90.
—— —— hydrogen, absorption of, in water, 98.
—— gas, electric spectra of metals in, 86.
Amylide, mercuric, action of zinc upon, 32.
Analysis of gases, on a new method of: by A. W. Williamson and W. J. Russell, 238.
—— organic, on a new combustion blow-pipe for: by W. Herapath, 49.
Anise, oil of, 5.
Aniline, action of chloride of cadmium on, 328.
Anniversary meeting of the Chemical Society (March 30, 1864), 435.
*Atherosperma Moschatum*, oil of, 5.
Atmolysis, 350.
Atomicities, on the classification of the elements in relation to their: by A. W. Williamson, 211.
Azophosphate of barium, 236.
—— copper, 235.
—— ferric, 234.
—— zinc, 236.
Azotised organic compounds, synthesis of, 48.

## B.

Baker, W., on the occurrence of nickel in lead, and its concentration by Pattinson's process, 377.
—— and Graham Stuart, on the existence of nitrogen in steel, 390.
Balance-sheet of the Chemical Society (1864), 445.
Barium, preparation of peroxide of, 267.
Baryta, on the action of, on suberic and azelaic acids: by R. S. Dale, 258.
Bassett, H., on the tetrabasic or orthocarbonate of ethyl, 198.
Bay, oil of, 5.
Benzoate of thallium, 151.
Benzoyl, peroxide of, 268.
Bergamot, oil of, 6.
Berthelot, M., on the synthesis of organic substances, 37.
Bimethyl-acetal, its existence in crude wood-spirit, 223.
Birch-bark, oil of, 7.
Bismuth, its action on mercuric ethide, 36.
—— occurrence of thallium in minerals containing, 143.
Blowpipe (combustion), on a new, for organic analysis, 49.
Blue Forest Marble, on the colouring matter of: by A. H. Church, 379.
Borate of thallium, 134.
Brass, its reflecting power for the chemical rays, 77.
Brine of salt meat, on the, and on the distribution of albumen through muscular tissue: by W. Marcet, 405.
Brodie, B. C., on the organic peroxides theoretically considered, 281.
—— on the peroxides of the radicles of the organic acids, 264.
Bromide of thallium, 138.
Butyl, peroxide of, 275.
Butylene-diamine, its formation by the action of hydrogen on cyanide of ethylene, 363.

## C.

Cadmium, its action on mercuric ethide, 36.
—— its reflecting power for the chemical rays, 77.
—— and thallium, simultaneous occurrence of, 144.
Cajeput, oil of, 7.
Calamus, oil of, 9.
Camphoryl, peroxide of, 277.

Caraway, oil of, 8.
Carbonate of ethyl, on the tetrabasic, by H. Basset, 198.
Carbonate of thallium, 133.
Carbonic acid and water, formation of organic substances from, 40.
Carbonic acid and carbonic oxide, electric spectra of metals in, 85.
Carbonic oxide and marsh gas, formation of propylene from, 45.
Cassia, oil of, 8.
Castor-oil plant, note on an alkaloïd contained in the seeds of the: by R. V. Tuson, 195.
Cedar-wood, oil of, 8.
Cedrat, oil of, 8.
Chemical nomenclature and notation, on: by A. W. Williamson, 421.
Chemical rays, absorption of, by reflection from polished surfaces, 76.
—— —— transmission through gases, 72.
—— —— liquids, 71.
—— —— solids, 62.
—— —— vapours, 72.
Chemical Society, Balance-sheet of the (1864), 445.
—— donations to the library of the (1864), 450.
—— proceedings at the meetings of the (1864), 433.
Chlorate of thallium, 140.
Chloride of iodine, its action on aniline, 328.
—— benzoic acid, 332.
—— carbazotic acid, 332.
—— orcin, 327.
—— phloridzin and salicin, 331.
Chlorides of thallium, 138.
Chlorine, electric spectra of metals in, 87.
Chlorobrominated ethylene, on, by Hugo Müller, 420.
Chlorophosphuret of nitrogen, analysis of, 230.
Chlorophosphuret of nitrogen, crystallized form of, 227.
Chlorophosphuret of nitrogen, on, and its products of decomposition: by J. H. Gladstone and J. D. Holmes, 225.
Chlorophyll, optical characters of, 314.
Chloropicrin, 154.
Chloroplatinate of triethyl-sulphethyl, 106.
Chromates of thallium, 142.
Church, A. H., on the colouring matter of blue forest marble, 379.
—— some experiments on the density of garnet, idocrase, &c., 386.
—— additional experiments on the density of certain minerals, 415.
Citrate of thallium, 151.
Citronella, oil of, 8.
Classification of the elements, on the, in relation to their atomicities: by A. W. Williamson, 211.
Cloves, oil of, 8.
Colloïdal substances, on the properties of silicic acid and other analogous: by Thomas Graham, 318.
Colophene, 19.
Coloured reflection, relation of, to absorption, 315.
Combustion-blowpipe for organic analysis, on a new: by W. Herapath, 19.
Combustion of iron in compressed oxygen, on the: by E. Frankland, 52.
Conington, F. T., obituary notice of, 435.
Constitution of matter, speculative ideas respecting the: by Thomas Graham, 368.
Copper, its action on mercuric ethide, 36.
—— carbon in, 184.
—— nitrogen in, 188.
—— on the non-metallic impurities of refined: by F. A. Abel, 164.
—— oxygen in, 166.
—— phosphorus in, 188.
—— its reflecting power for the chemical rays, 77.
—— selenium in, 186.
—— sulphur in, 187.
—— and thallium, alloy of, 146.
Coriander, oil of, 9.
Creatine and creatinine, preparation of, from the brine of salt meat, 106.
Crookes, W., on thallium, 112.
Cubebs, oil of, 9.
Cumenyl, peroxide of, 273.
Cyanate of thallium, 148.
—— of ethylene, action of nascent hydrogen on, 363.
Cyanide of thallium, 148.
Cyanoform, action of nascent hydrogen on, 364.
Cyanogen, action of nascent hydrogen on, 363.
—— electric spectra of metals in, 87.

D.

Dale, R. S., on the action of baryta on suberic and azelaic acids, 258.
Dancer, W., on the constitution of wood-spirit, 222.
Deutazophosphate of barium, 233.
—— zinc, 233.
Diactinic power of gases and vapours, 73.
—— liquids, 71.
—— solids, 64.

M.

Magnesium, electric spectrum of, 81.
Malate of thallium, 150.
Manganese, a contribution to the history of the oxides of, by W. Dittmar, 294.
Manganese, occurrence of thallium in minerals containing, 143.
Marble, Blue Forest, on the colouring matter of, by A. H. Church, 379.
Marcet, W., Remarks on the brine of salt meat, and on the distribution of albumen through muscular tissue, 405.
Marignac's oil, 156.
Marsh gas and carbonic oxide, formation of propylene from, 45.
—— conversion of, into ethylene, 43.
electric spectra of metals taken in, 85.
formation of acetylene from, 43.
—— formation of, from sulphide of carbon and sulphuretted hydrogen, 40.
—— naphthalene from, 44.
Matter, speculative ideas respecting the constitution of: by Thomas Graham, 368.
Meat, on the brine of salt, 405.
Meetings of the Chemical Society, Proceedings at the (1864), 433.
*Melaleuca ericifolia*, oil of, 10.
—— *linarifolia*, oil of, 10.
Mercuric amylide, action of zinc upon, 32.
- ethide, action of various upon, 35.
- ethide, action of zinc upon, 31.
- methide, action of zinc upon, 30.
Mercury, electric spectrum of, 81.
—— its reflecting power for the chemical rays, 77.
—— and thallium, amalgam of, 146.
Metals, action of various, on mercuric ethide, 35.
Metastannic acid, liquid, 325.
Methide, mercuric, action of zinc upon, 30.
Methyl, on the identity of, with hydride of ethyl: by C. Schorlemmer, 262.
Methylamine, formation of, by the action of nascent hydrogen on cyanogen, 363.
Methyl-chlorhydric ether, formation of, from marsh-gas, 42.
Methylic alcohol, synthesis of, 42.
Miller, W. A., on the photographic transparency of various bodies, and on the photographic effects of metallic and other spectra obtained by the electric spark, 59.
Mills, E. J., on nitro-compounds, 153.
Minerals, additional experiments on the density of certain: by A. H. Church, 415.
Mint, oil of, 11.
Mitscherlich, E., obituary notice of, 440.
Mixed gases, on the absorption of in water: by W. M. Watts, 88.
—— diffusion of into a vacuum, with partial separation, 350.
Molybdic acid, liquid, 326.
Monocarbon acids, their conversion into dicarbon acids, 109.
Mordenite, on, a new mineral from the trap of Nova Scotia: by Prof. How, 100.
Morindone, note on: by John Stenhouse, 333.
Müller, Hugo, on a new formation of malonic and succinic acids, 109.
—— on the preparation of monochloracetic and dichloracetic acids, 398.
—— on chlorobrominated ethylene, 420.
Muscular tissue, on the distribution of albumen through: by W. Marcet, 405.
Myrrh, oil of, 11.
Myrtle, oil of, 11.

N.

Naphthalene, formation of, from marsh-gas, 44.
Neroli, oil of, 11.
Nickel, on the occurrence of in lead, and its concentration, by Pattinson's process: by W. Baker, 377.
Nitraniline, 160.
Nitrate of thallium, 141.
Nitrate of triethyl-sulphyl, 105.
Nitrobenzol, 158.
Nitro-compounds, on: by E. J. Mills, 153.
Nitrogen, on the existence of, in steel: by Graham Stuart and W. Baker, 390.
—— and oxygen, diffusion of, into a vacuum, 351.
—— analysis of chlorophosphuret of, 230.
—— crystalline form of chlorophosphuret of, 227.
on chlorophosphuret of, and its products of decomposition: by J. H. Gladstone and J. D. Holmes, 225.
—— electric spectra of metals in, 87.
—— protoxide of, photographic electric spectra of metals in, 86.
Nitrosogens, 162.

Nomenclature and notation, on chemical: by A. W. Williamson, 421.
Nutmeg, oil of, 11.

O.

Obituary notice of F. T. Conington, 435.
—— E. Mitscherlich, 440.
—— H. Rose, 437.
—— W. Stark, 436.
Oefele, A. v., on a new class of organic sulphur-compounds, 105.
Oil, essential of, anise, *Atherosperma Moschatum* bay, 5.
—— bergamot, 6.
—— birch-bark, cajeput, calamus, 7.
—— caraway, cascarilla, cassia, cedar-wood, cedrat, citronella, cloves, 8.
—— coriander, cubebs, dill, elder, 9.
—— *Eucalyptus amygdalina*, *E. oleosa* Indian geranium, lavender, lemon, lemon-grass, *Melaleuca ericifolia*, *M. linarifolia*, 10.
—— mint, myrtle, myrrh, neroli, nutmeg, 11.
—— orange-peel, parsley, patchouli, peppermint, 12.
—— *petit grain*, rose, rosemary, rose-wood, santal-wood, thyme, 13.
—— turpentine, verbena, winter-green, wormwood, 14.
Oils, crude essential, physical properties of, 2.
—— refractive indices and specific gravities of, 3.
—— on essential: by J. H. Gladstone, 1.
—— essential, hydrocarbons obtained from, 17.
Olefiant gas, see Ethylene.
Oolitic iron ore, on the occurrence of vanadium in pig-iron smelted from the Wiltshire: by E. Riley, 21.
Optical properties of bodies, on the application of, to the detection and discrimination of organic substances: by G. G. Stokes, 304.
Orange-peel, oil of, 12.
Orcin, action of chloride of iodine on, 327.
Organic acids, on the peroxides of the radicles of the: by B. C. Brodie, 266.
—— analysis, on a new combustion blowpipe for: by W. Herapath, 49.
—— compounds of thallium, 148.
—— peroxides, on the, theoretically considered: by B. C. Brodie, 281.
Organic substances, on the detection and discrimination of, by their optical properties: by G. G. Stokes, 304.
—— substances, on the synthesis of: by M. Berthelot, 37.
—— sulphur-compounds, on a new class of: by A. v. Oefele, 105.
Orthocarbonate of ethyl, on the: by H. Bassett, 198.
Oxalates of thallium, 150.
Oxaniline, on: by R. Schmidt, 194.
Oxides of manganese, a contribution to the history of the: by W. Dittmar, 294.
Oxides of thallium, 128.
Oxygen, on the combustion of iron in compressed: by E. Frankland, 52.
—— electric spectra of metals in, 87.
—— and hydrogen, diffusion of, into a vacuum, 350.
—— nitrogen, 351.

P.

Paratartrate of thallium, 151.
Patchouli, oil of, 12.
Peppermint, oil of, 12.
Peroxide of acetyl, 272.
—— barium, preparation of, 267
—— benzoyl, 268.
—— butyl, 275.
—— camphoryl, 277.
—— cumenyl, 272.
—— thallium, 132.
—— valeryl, 276.
Peroxides, on the organic, theoretically considered: by B. C. Brodie, 281.
—— on the, of the radicles of the organic acids: by B. C. Brodie, 266.
Petit grain, oil of, 13.
Phipson, T. L., description of an apparatus for generating sulphuretted hydrogen, 152.
Phloridzin, action of chloride of iodine on, 331.
Phosphate of thallium, 135.
Phosphide of thallium, 135.
Phosphorus in Wiltshire pig iron (grey), 22, 23.
Photographic effects of the electric spectra of different metals in air, 78.
—— —— produced by transmitting the sparks through gases other than atmospheric air, 83.
Photographic transparency of bodies, on the, &c.: by W. A. Miller, 59.
Pig-iron, on the occurrence of vanadium in, smelted from the Wiltshire oolitic iron ore: by E. Riley, 21.

Pig-iron (grey) from Seend and Westbury in Wiltshire, silicium, sulphur, and phosphorus in, 22, 23.

Platinum, its reflecting power for the chemical rays, 77.

- and thallium, alloy of, 147.

—— —— double chloride of, 147.

Potassium, sulphydrate of, its action on acetic ether: by J. H. Wanklyn, 418.

Price, D. S., on the quantitative determination of sulphur, 51.

Proceedings at the meetings of the Chemical Society (1861), 433.

Propylene, formation of, from marsh-gas and carbonic oxide, 15.

Protoxide of nitrogen, electric spectra of metals in, 86.

Protoxide of thallium, 128.

Purpurin and alzarin, distinctive spectra of, 305.

Pyrites, preparation of thallium from, in the wet way, 117.

—— burners, preparation of thallium from the flue-dust of, 118.

R.

Radicles of the organic acids, on the peroxides of the: by B. C. Brodie, 266.

Rays, absorption of chemical, by reflection from polished surfaces, 76.

—— transmission through gases, 72.

—— liquids, 71.

—— solids, 62.

—— vapours, 72.

Reflection, coloured, relation of, to absorption, 315.

Report of the President and Council, 435.

—— Treasurer, 445.

*Ricinus communis*, or castor-oil plant, note on an alkaloid contained in the seeds of the: by R. V. Tuson, 195.

Riley, E., on the occurrence of vanadium in pig-iron smelted from the Wiltshire oolitic iron ore, 21.

Rose, H., obituary notice of, 437.

Rose, oil of, 13.

Rosemary, oil of, 13.

Rosewood, oil of, 13.

Russell, W. J., and A. W. Williamson, on a new method of gas analysis, 238.

S.

Salicin, action of chloride of iodine on, 331.

Saline residues of the salt works at Nauheim, preparation of thallium from, 119.

Salt meat, on the brine of, by W. Marcet, 405.

Santal-wood, oil of, 13.

Schmidt, R., on oxaniline, 194.

Schorlemmer, C., on the identity of methyl and hydride of ethyl, 262.

Seend iron ore, analysis of, 28.

Selenide of thallium, 137.

Sesquichloride of thallium, 139.

Silicates alkaline, decomposition of, by diffusion, 324.

Silicic acid, alcogel of, 322.

—— alcosol of, 321.

—— etherogel of, 322.

—— glycerogel and glycerosol of, 322.

—— hydrogel and hydrosol of, 321.

—— pectization of, 319, 324.

—— sulphogel of, 323.

—— on the properties of, and of oth , analogous colloidal substances: b Thomas Graham, 318.

Silicium in Wiltshire pig-iron (grey), 22, 23.

Silver, its action on mercuric ethide, 36.

—— its reflecting power for the chemical rays, 77.

—— relative absorptive action of various media upon the electric spectrum of 76.

Sodium, action of, on valerianate of et 371.

Solids, diactinic power of, 61.

Spectra of alloys, 82.

—— on the photographic effects of metallic and other, obtained by means of the electric spark: by W. A. Miller, 59.

Spectrum, electric, of carbon, relative absorptive action of various media upon the, 76.

—— of thallium, 134.

Speculative ideas respecting the constitution of matter: by Thomas Graham, 368.

Speculum metal, its reflecting power for the chemical rays, 77.

Stannic acid, liquid, 325.

Stark, W., obituary notice of, 436.

Steel, on the existence of nitrogen in, by Graham Stuart and W. Baker, 390.

—— its reflecting power for the chemical rays, 77.

Stenhouse, J., on the action of chloride of iodine on certain organic substances, 327, 366.

———— note on morindone, 333.

Stokes, G. G., on the application of the optical properties of bodies to the

detection and discrimination of organic substances, 304.
Stuart, Graham, and W. Baker on the existence of nitrogen in steel, 390.
Sulphate of triethyl-sulphyl, 106.
Sulphates of thallium, 136.
Sulphydrate of potassium, action of, on acetic ether: by J. A. Wanklyn, 408.
Sulphide of thallium, 135.
Sulphocyanide of thallium, 148.
Sulphur in Wiltshire pig-iron (grey), 22, 23.
—— preparation of thallium from, in the wet way, 117.
—— on the quantitative determination of: by D. S. Price, 51.
—— tetratomic and hexatomic, 106.
Sulphur-compounds, on a new class of: by A. v. Oefele, 105.
Sulphuretted hydrogen, description of a new apparatus for generating: by T. L. Phipson, 152.
—— —— electra spectra of metals in, 86.
Synthesis of organic substances, on the: by M. Berthelot, 37.

T.

Tartrates of thallium, 150.
Terchloride of thallium, 140.
[illegible]eriodorcin, 327.
Tetrabasic or ortho-carbonate of ethyl, on the: by H. Bassett, 198.
Tetrylene-triamine, its formation by the action of nascent hydrogen on cyanoform, 361.
Thallium, on: by W. Crookes, 112.
—— and aluminium, 142.
—— bismuth, 113.
—— boron, 134.
—— bromine, 138.
—— cadmium, 141.
—— carbon, 133.
—— chlorine, 138.
—— chromium, 142.
—— copper, 146.
—— gold, 147.
—— hydrogen, 132.
—— iodine, 145.
—— iron, 145.
—— lead, 145.
—— manganese, 143.
—— mercury, 146.
—— nitrogen, 141.
—— oxygen, 128.
—— platinum, 147.
—— phosphorus, 135.
—— selenium, 137.
—— sulphur, 135.
Thallium and tin, 145.
—— zinc, 144.
—— acetate of, 149.
—— aqueous oxide of, 130.
—— atomic weight of, 125.
—— benzamide, 151.
—— benzoate of, 151.
—— bichloride of, 140.
—— borate of, 134.
—— bromide of, 138.
—— carbonate of, 133.
—— chlorate of, 140.
—— chlorides of, 138.
—— chromates of, 142.
—— citrate of, 151.
—— combustion of, 123.
—— cyanate of, 148.
—— cyanide of, 148.
—— diamagnetism of, 125.
—— electric conductivity of, 125.
—— —— spectrum of, 81, 121.
—— ethylate of, 149.
—— ferri- and ferro-cyanide of, 148.
—— formate of, 148.
—— green line in spectrum of, 124.
—— history of, 115.
—— hydrated oxide of, 130.
—— hyposulphite of, 136.
—— iodide of, 137.
—— malate of, 150.
—— memoirs relating to, 112.
—— nitrate of, 141.
—— organic compounds of, 148.
—— oxalates of, 150.
—— oxides of, 128.
—— paratartrate of, 151.
—— peroxide of, 132.
—— phosphate of, 135.
—— picrate of, 151.
—— position of, in metallic series, 126.
—— preparation of, from commercial hydrochloric acid, 118.
—— —— flue-dust of pyrites-burners, 118.
—— —— iron pyrites, 116.
—— —— the saline residues of the salt-works at Nauheim, 117.
—— —— sulphur or pyrites in the wet way, 117.
—— protochloride of, 138.
—— protoxide of, 128.
—— purification of, 119.
—— reduction of, 125.
—— salts of, 131.
—— selenide of, 137.
—— sesquichloride of, 139.
—— sources of, 115.
—— specific gravity of, 122.
—— sulphates of, 136.
—— sulphides of, 135.
—— sulphocyanide of, 148.
—— tartrates of, 150.

Thallium, terchloride of, 140.
—— urate of, 151.
—— valerate of, 151.
Thudichum, J. L. W., researches on the physiological variations of the quantity of hippuric acid in human urine, 55.
Thyme, oil of, 13.
Tissue, on the distribution of albumen through muscular: by W. Marcet, 405.
Titanic acid, liquid, 325.
Transparency, on the photographic, of various bodies, &c., by W. A. Miller, 59.
Triethyl-sulphyl, 105.
Trinitroglycerin, 158.
Tube atmolyser, 355.
Tungstic acid, liquid, 325.
Turpentine, oil of, 14.
Tuson, R. V., note on an alkaloïd contained in the seeds of the *Ricinus communis* or castor-oil plant, 195.

U.

Urate of thallium, 151.
Urine, researches on the physiological variations of the quantities of hippuric acid in human: by J. L. W. Thudichum, 55.

V.

Valerate of thallium, 151.
Valeryl, peroxide of, 276.
Valeryl, liberation of, by the action of sodium on valerianate of ethyl, 371.
Vanadium, on the occurrence of, in pig-iron, smelted from the oolitic iron ore, 21.
Verbena, oil of, 14.

W.

Wanklyn, J. A., on the action of sodium on valerianate of ethyl, viz., the liberation of the acid-forming radicle, valeryl, 371.
Wanklyn, J. A., on a curious example of etherification, 367.
——— on the nature of the compound ethers, 401.
——— on the action of sulphydrate of potassium on acetic ether, 418.
——— and E. Erlenmeyer, on the hexyl group, 190.
Water, absorption of ammonia and air in, 90.
—— —— ammonia and hydrogen, 98.
—— —— sulphurous acid and carbonic acid in, 98.
Water and carbonic acid, formation of organic substances from, 40.
Watts, W. M., on the absorption of mixed gases in water, 88.
Williams, C. Gr., on acetanilide, 106.
Williamson, A. W., on the classification of the elements in relation to their atomicities, 211.
——— remarks on chemical nomenclature and notation, 421.
——— and W. J. Russell, on a new method of gas analysis, 238.
Wiltshire oolitic iron ore, on the occurrence of vanadium in pig iron smelted from, by E. Riley, 21.
Winter-green, oil of, 14.
Wood-spirit, on the constitution of, by W. Dancer, 222.
Wormwood, oil of, 14.

Z.

Zinc-amyl, 33.
—— amylate of, 34.
—— amylochloride of, 34.
—— amyloiodide of, 35.
—— its action on mercuric amylide, 32.
—— its action on mercuric ethide, 31.
—— —— methide, 30.
—— its reflecting power for the chemical rays, 77.
Zinc-compounds of the alcohol-radicles, on a new reaction for the production of the, by E. Frankland and B. F. Duppa, 29.

657 Ex

---

PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE